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Ford

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Automotive Emissions and
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Environmental and Safety
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Ford Motor Company
The American Road
Dearborn, Michigan 48121

July 23, 1990

Air Docket (LE-131)
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, DC 20460

Attention: Docket No. A-90-16

The information provided with this communication reflects Ford Motor Company's comments on the June 5, 1990 Federal Register Notice regarding the May 9, 1990 Ethyl Corporation ("Ethyl") submittal of an application for a waiver of the prohibition on fuels and fuel additives set forth in Section 211(f) of the Clean Air Act, specifically for 1/32 gram/gallon (gm/gal) methylcyclopentadienyl manganese tricarbonyl (MMT). Comments regarding the aforementioned waiver application were requested to be submitted to EPA on or before July 22, 1990.

We have reviewed the results of Ethyl's most recent test program which was conducted in support of their subject waiver request. This program demonstrated the characteristic hydrocarbon increase which has been previously attributed to MMT. The results also exhibited an unexplained decrease in carbon monoxide and oxides of nitrogen emissions.

We have also examined the results of previous studies which have shown that, at higher concentrations (1/8 and 1/16 gm MMT/U.S. gal), MMT has a deleterious effect on vehicle emission control systems. In view of these incongruous findings, there is a particular need to demonstrate conclusively that similar effects will not be realized from MMT at the concentration proposed in the waiver request.

To approve the waiver, we believe that the following would have to be determined:

- that specific inspection and analysis of these components show the EGO sensors and catalysts on the tested vehicles were not adversely affected by the MMT;

- why the adverse effects that were clearly demonstrated at 1/8 and 1/16 gm MMT/U.S. gal gasoline are not so readily apparent in the 1/32 gm MMT/U.S. gal gasoline test fleet -- including an evaluation of the lack of additive packages in the test fuel; and

- that the 1/32 gm MMT/U.S. gal added to commercial grade gasoline containing standard additive packages (as opposed to the clear fuel used in Ethyl mileage accumulation) will not cause or contribute to the failure of a vehicle to comply with any applicable standard, including the standards that will take effect pursuant to imminent Clean Air Act amendments.

The attached text contains the in-depth discussion of these concerns and recommended test procedures.

Sincerely,

D. R. Buist for

Attachments

cc: Ms. Mary T. Smith, Director
Field Operations and Support Division (EN-397F)
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, DC 20460

FORD MOTOR COMPANY'S COMMENTS IN RESPONSE TO ETHYL CORPORATION'S APPLICATION FOR WAIVER TO ALLOW METHYLCYCLOPENTADIENYL MANGANESE TRICARBONYL (MMT) AT 1/32 GRAM MMT/U.S. GALLON UNLEADED GASOLINE

Docket No. A-90-16

On May 9, 1990, Ethyl Corporation submitted a request for waiver to allow the use of MMT (marketed as HiTEC 3000) at the concentration of 1/32 gram (gm) MMT/U.S. gallon (gal) unleaded gasoline. Pursuant to this request, Ethyl has provided the results of an extensive test program which accumulated 75,000 miles on each of 48 vehicles, half of these being operated with the 1/32 gm MMT/gal added to the test fuel, to determine the effect of MMT on vehicle exhaust systems.

There has not been any information presented pertaining to chemical or physical analyses performed on the components of the emission system (i.e., catalyst, EGO sensor, fuel injectors, etc.). These tests could provide conclusive evidence regarding the effects of MMT on vehicle emission control systems. Further, although the test program provided some valuable information regarding the effects of MMT on exhaust emissions, it also raised several new concerns. We believe that these concerns need to be resolved, by the test procedures which are outlined below, before the waiver can be approved.

The following materials present our findings on analysis performed on catalysts from vehicles which were operated on fuel containing MMT (1/16 gm/gal), our concerns regarding the test protocol, and finally, our recommendations for the test procedures discussed above.

Ford Experience with MMT

Ford has just completed an analysis of 11 catalysts removed from Ford of Canada employee vehicles which have been operated on fuel permitted to contain MMT at a concentration of 1/16 gm MMT/U.S. gallon gasoline (refer to Attachment 1). The purpose of this investigation was to determine if the effects of MMT at a concentration of 1/16 gram MMT/U.S. gallon have a measurable effect on the emission control systems of vehicles which have not encountered a malfunction.

The results of this study indicate that the combustion product of MMT, Mn_3O_4, was the primary cause for the significant decreased efficiency of these catalysts (only trace amounts of other oxides of manganese were found on the catalysts). A 5 to 80-micron thick layer of Mn_3O_4 covered the washcoat and contributed to the mass transfer resistance, thus decreasing the efficiency of the catalyst for converting HC and to lesser degree, NO_x and CO. The analytical data also showed that as mileage increased, the amount of manganese deposited on the catalyst washcoat also increased.

The above findings support those from previous analyses which were conducted on 41 catalysts from Canadian vehicles which were exposed to fuel permitted to contain 1/16 gm MMT/U.S. gal gasoline (refer to Attachments 2 & 3). These vehicles were returned for diagnostics because of poor driveability, and one or more malfunctioning components were discovered including the catalyst. Physical and chemical analyses of these catalysts have shown severe (5 to 30 microns) Mn_3O_4 buildup occurred on the catalyst washcoat. This Mn_3O_4 layer slowed the diffusion of the gas to the washcoat so that the conversion rates were reduced as mass transfer through the Mn_3O_4 layer became the rate controlling step. Over time, this layer would continue to thicken, further deteriorating catalyst efficiency. In severe cases, the Mn_3O_4 deposits blocked the cells of the catalyst, restricting the exhaust gas flow through the catalyst, creating increased back pressure, and in turn, poor driveability.

In conjunction with the 41-catalyst analysis, a catalyst was removed from a randomly-selected, well-maintained Ontario Provincial police car (5.8L 1978 LTD 58,120 miles, refer to Attachment 2). Analysis of this catalyst showed substantial inlet face plugging and significant catalyst efficiency deterioration for all three pollutants, HC, CO and NO_x. Although there were no apparent driveability performance problems observed for this vehicle, the contaminated catalyst exhibited nearly total loss in NO_x conversion.

Although the problems we have experienced in our emission control systems, as described above, have occurred in cars exposed to levels of MMT twice that which are being proposed under the waiver request, it is clear that reduced MMT concentration will not eliminate combustion by-products, but will merely alter the rate of formation. Because the catalyst acts as a filtration system and removes most of the Mn_3O_4 which has not deposited on the combustion chamber or in the exhaust manifold, we believe the effects of MMT are proportional to its concentration in the fuel.

This proportionality was discussed in the SAE paper (790704), "Results of Coordinating Research Council MMT Field Test Program" (Attachment 4). The 63 vehicles tested in the field program used a fuel representative of a commercial gasoline for mileage accumulation (clear gasoline was used only for the emission tests). Comparisons of the vehicle emissions from the three sets of cars that comprised this fleet (containing 0 MMT, 1/16 gm MMT/gal and 1/32 gm MMT/gal) show that hydrocarbon conversion efficiencies decrease with increased MMT concentration. In addition, no evidence of decreases in CO or NO_x emissions were observed in this test program.

Concerns Regarding Test Protocol:
Howell EEE fuel, used exclusively for exhaust and evaporative emission testing, was employed in the test program for mileage accumulation. However, under 40 CFR §86.113-90(a)(1), mileage accumulation fuels must be "representative of commercial gasoline which will be generally available through retail outlets". Such fuels, accordingly, contain deposit control additive packages to prevent deposit build-up in engines, injectors, and other components. Howell EEE does not contain these additives and is therefore not representative of commercially-available gasoline. Lack of fuel detergents would cause an increase in the combustion chamber or intake fuel system deposits and thereby result in an unrepresentative baseline as a reference point. Therefore, there is some reason to suspect the representativeness of Ethyl's data regarding the relative effects of MMT on in-use vehicles or to certification test vehicles. (Attachment 5, Figures 1-3)

We have compared the test program emission data for the Ford baseline vehicles to our own 50k durability data for cars of the same model and engine family. The cars operating on Howell EEE have substantially higher emission levels for both hydrocarbons and carbon monoxide. NO_x emissions are also substantially different.

Another concern is that averaging the effects of MMT over the entire test fleet yields different conclusions than viewing individual vehicles. For example, although fleet average CO and NO_x emissions are shown to be reduced through the use of MMT, four of the eight models tested have higher CO emissions and two of the eight have higher NO_x emissions for the first 50,000 miles when operated with MMT. In fact, many of the significant gains in vehicle emissions are not realized until after high mileages have been accumulated. These transitions at high mileage often tend to coincide with completion of repairs, routine maintenance or, possibly, other systematic problems and should be analyzed further. (Attachment 5; Table 1, Figures 4-27)

Concern over Effects on Vehicle Emissions

It has been suggested that the data resulting from the MMT test program demonstrate that addition of MMT results in reduced NO_x and CO emissions. Although hydrocarbon emissions were found to increase slightly (approximately 6% over 1,000 to 50,000 miles) it is claimed that this increase will not contribute to vehicle failure to meet the current HC emission standard of 0.41 gm/mile. However, there is no reason to believe that all vehicles will operate within the same compliance safety margin in customer hands. In addition, as mentioned above, although the 6% increase is the fleet average increase in HC emissions, some vehicle models exhibit substantially higher increases. Thus, the ability to meet proposed future HC standards may be sharply inhibited for the manufacturers of those vehicles.

There appears to be no definitive explanation for the NO_x reduction. It has been suggested that it may be due to the catalytic behavior of the MMT combustion product, manganese oxide (Mn_3O_4), which admittedly coats the interior of the exhaust system. Although Mn_3O_4 does indeed have the ability to catalytically decompose NO_x, it is highly unlikely that this is the cause for the reduced emission levels. Catalytic decomposition of NO_x by Mn_3O_4 is known to be too slow to be practical at the NO_x levels found in automotive exhaust. Thus, no technical support is evident for the enhanced reductions in NO_x.

There are, however, many other possible explanations for the NO_x reduction. These include:

- Mn_3O_4 deposits in the combustion chamber create "hot-spots" which affect the ignition point and serve to both decrease NO_x and increase HC;

- oxygen sensors coated with Mn_3O_4 can change the engine air/fuel mixture from that intended by the engine design;

- Mn_3O_4 deposits on the fuel injectors may alter the spray patterns and/or prevent closure, thus increasing enrichment in one or more cylinders, leading to increased HC emissions, subsequently decreased NO_x, and possible imbalance in engine power generation;

- Mn_3O_4 deposits on the catalyst washcoat can lead to increased backpressure which will increase residual gas in the engine, thus increasing HC emissions and decreasing NO_x emissions and possibly affect vehicle performance.

It is this uncertainty in the mechanism for NO_x reduction which makes a greater in-depth analysis so critical in order to determine what is occurring within the vehicle emission control system. Some insight to this mechanism may be derived from the comparison of the constituents of the feed-gas to the tail-pipe emissions (Attachment 5, Table 2). Although very little engine-out data were provided in the waiver documents, from the few tables provided, the trend of increased HC and decreased NO_x, which is seen in the tailpipe and attributed to the activity in the catalyst, is present in the engine-out gas. This observation indicates that emission reductions for NO_x and CO occur prior to the catalyst and are, therefore, unlikely to be the result of the catalytic characteristics of Mn_3O_4, but rather attributed to the mechanisms proposed above. SAE paper 790704, discussed above, further supports this conclusion.

The emission data from this extensive test program gave no evidence that MMT caused reductions in either CO or NO_x emissions.

Moreover, we are concerned over the observed increase in hydrocarbon emissions. This percent increase is significant, particularly in light of the lower standards and doubling of the useful life compliance period proposed by Congress under pending Clean Air Act legislation that is expected to be enacted shortly. It has been stated that future emission requirements do not have to be considered as a matter of law in the EPA evaluation of this waiver request. Rather, compliance with existing standards need only to be considered. However, hydrocarbons are key ozone precursors, and it is the congressional concern for ozone problems which have prompted the legislative activity. Thus, it is inappropriate to ignore the legislative proposal that, starting with the 1993 model year, some of our cars will have to comply with a hydrocarbon standard of 0.25 gm/mile, a 39% reduction over current levels. Pending legislation also could reduce the hydrocarbon standard by an additional 50% by 2004 (0.125 gm/mile). It would be impractical to ignore the effects of MMT on emission levels in light of the reductions which are proposed for the near future before introducing this additive to vehicle fuels. In fact, the law is silent on the issue of future emissions standards. Therefore, EPA is clearly not precluded from considering this issue and in view of the virtual certainty of more stringent standards, we believe it would be inappropriate for EPA to grant a fuel waiver without considering its effect on the standards likely to be in effect when the waiver would be operative.

We would also like to emphasize that a waiver should be granted only if it is determined that the fuel or additive will not cause or contribute to the failure of vehicles to comply with any applicable emission standard. It is not sufficient basis to grant a waiver if EPA determines no such effect on NO_x or CO emissions, but that the fuel or additive would cause or contribute to the failure to comply with HC standards.

Although improvements will be made in emission control systems in anticipation of these standards, MMT can be expected to aggravate the exhaust emissions in meeting the Tier I standards and compliance will be severely affected. In order to meet the proposed Tier I standards, the control system will have to maintain a tight air/fuel ratio (minimum amplitude and short duration of deviations in stoichiometry). This is possible only if both the emission and control systems are kept clean during the mandatory in-use compliance period. Any plugging of injectors or EGO sensors, or deposits on the catalyst, will cause a lean shift and slow response from the oxygen sensor and increase the diffusion barrier on the catalyst. Therefore, the emission control systems of the future will have an increased sensitivity to Mn_3O_4 deposits and any increase in engine-out emissions will have a larger percentage effect on tailpipe emissions.

In addition, promising advances in emission control technology has indicated emission benefits through the use of close-coupled catalysts. These catalysts, however, would be operating at higher temperatures, hence increasing their susceptibility to Mn_3O_4 deposits. Therefore, a hydrocarbon emissions could increase despite improved technology if MMT is included in vehicle fuel.

We are also concerned that we have seen no data regarding the effect of MMT on emissions of light-duty trucks. These vehicles comprise a fast-growing portion of the American vehicle fleet, and are also subject to pending reduced emission standards. Light trucks run "hotter" than passenger vehicles, which may lead to performance problems if MMT is added to the fuel. Mn_3O_4 is known to plate-out fast in hot environments so that buildups will develop faster in light trucks than in passenger vehicles.

Evaporative emissions also need to be considered. The effects of fuel composition on the evaporative emissions control system become more critical with the stringent test procedures recently proposed. An assessment of the effects of MMT on canister storage capacity and canister purge may be warranted.

Finally, we are concerned about the emissions of Mn_3O_4 which will result from the introduction of MMT in gasoline. Our analysis has indicated that approximately only 24% of the Mn_3O_4 formed by the combustion of MMT will be deposited on the catalyst. The remaining 76% is either deposited in the exhaust system or emitted into the environment. We have become increasingly aware of the composition of vehicle exhaust and the pending standards to control their release into the environment. Therefore, we are apprehensive regarding the addition of toxic Mn_3O_4 to our emissions at unknown levels.

<u>Recommendations for Further Evaluation</u>

We believe that a key factor in the determination of the effects of MMT is the post-mortem analyses of the components of the emission control system, in particular the catalyst and oxygen sensor from the test vehicles which have been operated on fuel containing MMT at the concentration of 1/32 gm MMT/U.S. gal gasoline. These analyses would include the following tests which should be performed on the catalytic converters and oxygen sensors after they have been removed and photographed:

- Analysis by x-ray fluorescence
- BET surface measurements
- Microprobe for contaminant depth profile
- Optical and scanning electron microscopic examination of the washcoat conditions
- Determination of catalytic converter efficiency by steady-state and light-off curves
- Determination of oxygen sensor efficiency by sensor response delay

Additionally, in order to determine the effects of MMT on actual, in-use vehicles, similar post-mortem tests should be conducted on catalytic converters removed at random from Canadian vehicles which have been exposed to MMT (similar to those used in Ethyl's test program). The analysis of catalytic converter attributes and performance (i.e., BET and efficiency) should sufficiently demonstrate the actual long-term effects of MMT on in-use catalytic converters. Although we realize that the concentration of MMT in the Canadian gasoline is twice that which is currently being proposed by Ethyl, we still believe that valuable information concerning the effects of MMT on emission control systems may be gathered from these tests.

The vehicles selected for these physical and chemical characterization tests should represent a statistically significant cross-section of all Canadian Provinces. The vehicles should have documented maintenance, driving, and fueling records. The analysis should be performed not only on the catalytic converters, but also on other emission components (i.e., oxygen sensors and fuel injectors) from each of the vehicles selected for testing.

Our final suggestion is to express our concern regarding the use of Howell EEE fuel for mileage accumulation in the baseline vehicles in their test program. As noted previously, this fuel, which lacks detergents, is not representative of commercially-available gasoline. To best discern the effects of MMT on vehicle emissions, the reference or baseline test cars should accumulate mileage on commercial gasoline and the second group tested with the same commercial fuel to which MMT was added.

Should this program actually be re-run with commercial-grade gasoline, we would further recommend that vehicles with the following be used to best simulate the emission control technology that will be available in the near future in compliance with proposed Tier I emission standards: mass air, dual EGOs, sequential electronic fuel injection (SEFI), and close-coupled catalysts. Although electrically heated catalysts are not yet ready for production, this technology may become necessary for compliance with proposed future stringent standards. Therefore, the effect of MMT on this catalyst technology should also be determined.

Furthermore, because the rate of Mn_3O_4 deposition is increased by high catalyst temperature, as well as laminar gas flow conditions prior to entering the catalyst, these features will have to be taken into account in the selection of the vehicles for the test fleet. Also, driving conditions which tend to raise catalyst temperature (i.e., engine loading) will have to be considered in order to determine the effects of MMT on in-use vehicles.

Recommendations to EPA

We do not believe that conclusive proof has been submitted to show that MMT will not cause or contribute to the failure of a vehicle to comply with the applicable standards. To the contrary, we believe that evidence exists that MMT combustion products will have a deleterious effect on the function of the emission control system. Therefore, we strongly recommend that EPA require additional testing and analysis of the effects of MMT on vehicle emission control systems before making their decision on this waiver request. To approve the waiver, we believe that the following would have to be demonstrated:

- that specific inspection and analysis of these components show the EGO sensors and catalysts on the tested vehicles were not adversely affected by the MMT;
- why the adverse effects that were clearly demonstrated at 1/8 and 1/16 gm MMT/U.S. gal gasoline are not so readily apparent in the 1/32 gm MMT/U.S. gal gasoline test fleet -- including an evaluation of the lack of additive packages in the test fuel; and
- that the 1/32 gm MMT/U.S. gal added to commercial grade gasoline containing standard additive packages (as opposed to the clear fuel used in Ethyl mileage accumulation) will not cause or contribute to the failure of a vehicle to comply with any applicable standard, including the standards that will take effect pursuant to imminent Clean Air Act amendments.

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LIST OF ATTACHMENTS

Attachment 1: Ford report presenting results of recent analyses of 11 catalysts removed from Ford of Canada employee vehicles (operated on fuel containing 1/16 gm MMT/U.S. gal gasoline). These catalysts exhibit coating by Mn_3O_4 and resultant severe loss of conversion efficiency which is proportional to vehicle mileage.

Attachment 2: Ford report which details the results of analyses performed on 26 catalysts removed under warranty from Canadian vehicles. These catalysts were found to be coated, and to some extent plugged, by Mn_3O_4. Catalyst efficiencies were severely reduced. Attached to this report are the results of analyses performed on the catalyst of a randomly selected Ontario Provincial Police car.

Attachment 3: SAE paper, "Characterization of Automotive Catalysts Exposed to the Fuel Additive MMT" (890582), presented by Ford Research. The report describes the findings of the analyses of 15 catalysts, also removed under warranty from Canadian vehicles. The findings were the same as those discussed above.

Attachment 4: SAE paper, "Results of Coordinating Research Council MMT Field Test Program" (790706), prepared by GM Research Laboratories, Exxon Company and Chevron Research Company. This study indicates that the use of MMT (at either 1/16 or 1/32 gm MMT/U.S. gal.) will increase HC emissions without effecting either CO or NO_x emissions.

Attachment 5: Detailed analysis of Ethyl's test data to determine the effects of MMT on individual models. The following tables and figures are included in this attachment:

- Table 1: Percent Effect of MMT over Baseline (Averaged over Range)
- Table 2: Effect of MMT on Engine-Out and Tailpipe Emissions at 50k and 75k
- Figures 1-3: Percent Difference - Ethyl Baseline versus Ford Certification Vehicle Emissions (HC, CO and NO_x)
- Figures 4-30: Effect of MMT on Vehicle Emissions - Models C, D, E, F, G, H, I and T (HC, CO and NO_x)

ATTACHMENT 1

FORD REPORT: ANALYSIS OF 11 CATALYSTS
FROM FORD OF CANADA EMPLOYEE VEHICLES

A-90-16
IV-D-59

Inter Office

Research Staff

July 20, 1990

To:	D. L. Kulp	H. S. Gandhi	L. M Roslinski
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	R. G. DeLosh	T. J. O'Brien	
cc:	D. R. Buist	H. Lenox	
	J. C. Gagliardi	M. A. Roberts	
	J. T. Huston		

Subject: Post Mortem Analysis of Catalysts from Canadian Vehicles Fueled with MMT-containing Gasoline.

SUMMARY

A series of catalysts taken from Ford of Canada employee vehicles have been physically and chemically characterized to determine the effects of the fuel additive MMT. The results indicate the the combustion product of MMT, Mn_3O_4, is the primary cause for the decreased efficiency of the catalysts. A 5 to 80 micron thick layer of Mn_3O_4 covers the washcoat and contributes to the deterioration of the catalyst efficiency. This layer in effect increases the mass transfer resistance and thus decreases the efficiency of the catalyst for converting HC and to lesser degrees, NO_x and CO. Analytical results show that the inlets of the catalysts have between 0.7 and 3.0 wt% Mn while contaminants such as Pb, P, Zn and S are presnet at lower concentrations and do not contribute significantly to the deactivation of the catalysts. The analytical data also shows that as mileage increases the amount of manganese also increases.

Results and Discussions

Catalysts from 10 Ford of Canada Employee vehicles (11 catalysts) were removed from their respective vehicles and submitted to Research for comprehensive chemical and physical characterization. These vehicles were randomly selected and had <u>no</u> reported mechanical or operational problems. These vehicles were 1987-1989 3.0L/3.8L Taurus/Sables having in-use mileages between 21,500 miles and 62,224 miles (Table 1). Each vehicle had been fueled with commercially available Canadian fuel presumably containing the fuel additive MMT at a concentration of 1/16 g Mn/gal, as allowed by Canadian law.

Table 1

Canadian Vehicles

Number	Vehicle	MY	Engine	Mileage
BK1	Taurus	1988	3.0L	35,733
BK2	Sable	1989	3.0L	28,840
BK3	Sable	1988	3.0L	44,235
BK4	Taurus	1988	3.0L	41,093
BK5	Sable	1988	3.0L	21,500
BK6	Taurus	1987	3.0L	48,174
BK7A*	Sable	1988	3.8L	62,224
BK7B*	Sable	1988	3.8L	62,224
BK8	Taurus	1987	3.0L	33,354
BK9	Sable	1988	3.0L	27,416
BK10	Taurus	1988	3.0L	39,662

* BK7A and BK7B refer to the 2 brick system on the 3.8L Engine class, right and left side (driver side), respectively

The as-received condition of each individual catalysts used in this evaluation are shown by the photographs contained in appendices A-J of this report. Visually, the interior of the converter housings were coated with a rust colored residual deposit. Further visual inspection of the ceramic monoliths also showed the outside and channels to be coated to varying degrees with the rust colored deposit. The inlets of the monoliths showed the heaviest amounts of the rust colored residue. Similarily, the outlets of the monoliths also exhibited the rust colored residue but to a lesser degree. X-Ray diffraction analysis of the deposit indicate it to be Mn_3O_4. Clogging of several of the channels were observed in samples BK1 (35,733 miles) and BK7A-7B (62,224 miles). None of the monoliths showed visual signs of exposure to abnormally high operating temperatures.

The results of x-ray fluorescence analysis of samples taken from each individual monolith are detailed in appendices A-J. A summary of the major contaminants along with the B.E.T. surface area values are shown in Table 2. Manganese concentrations, as expected, are highest at the inlet of the monoliths and decrease toward the outlet. Manganese concentration at the inlets ranged from a low of 0.79 wt% to a high of 3.23 wt%. This data is graphically summarized in figure 1 and shows that as mileage increases the concentration of Mn also increases. It is important to note that other contaminants such as Pb, S, P, and Zn are all within normal ranges for these levels of accumulated in-use mileage.

Optical micrographs of each of the catalysts are shown in appendices A-J. The inlet channels of the monoliths have a layer of residue varying in thickness covering the washcoat. Based on the optical micrographs at 80X, estimates of the thickness vary from approximately 5 microns on the ribs to approximately 30 microns on the filet area of the monoliths. In some cases the thickness of the layer is estimated at 10 times greater than the washcoat thickness.

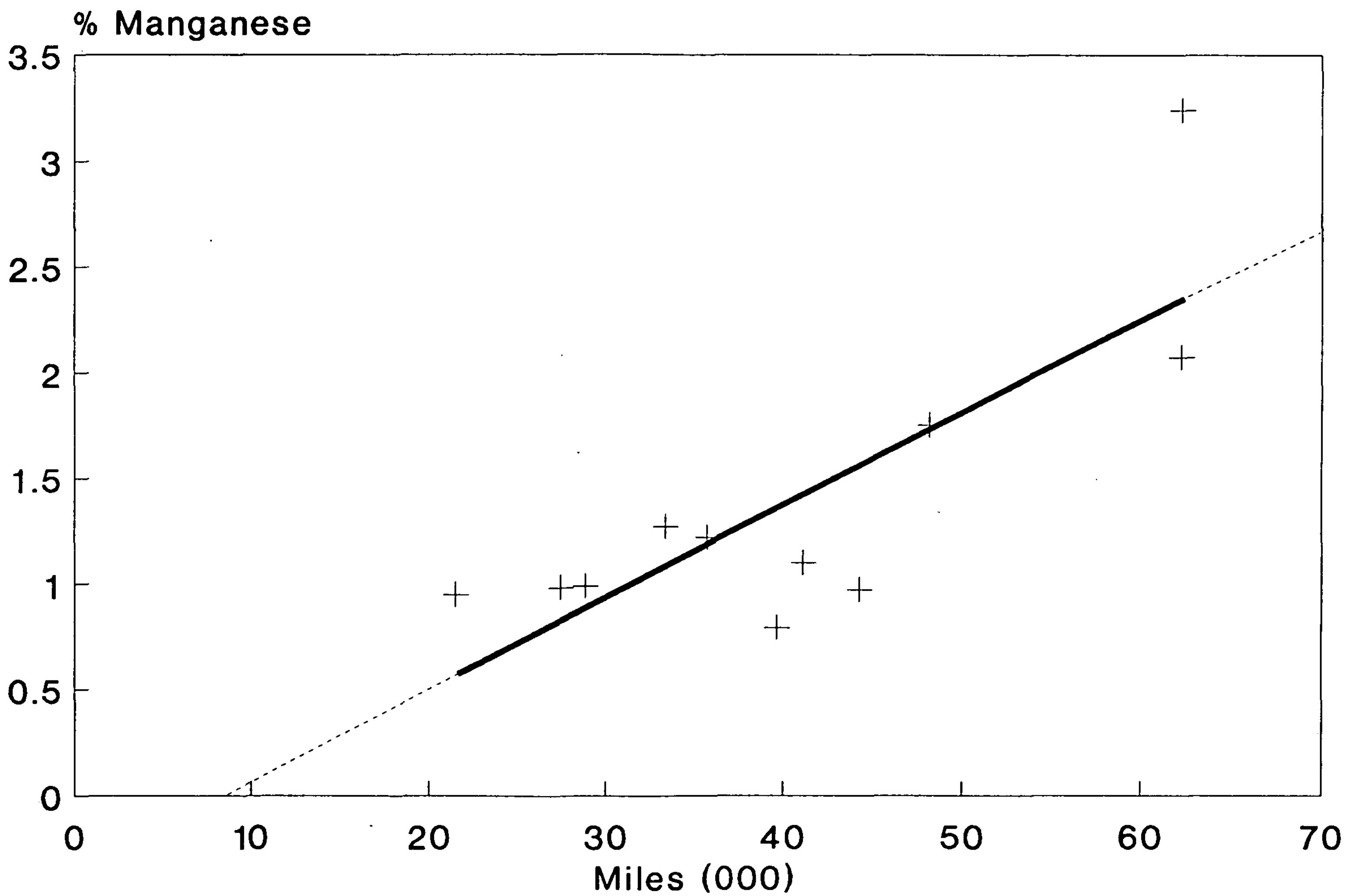


Figure 1- X-ray Fluorescence Analysis of Catalyst versus Vehicle Mileage

Table 2

ELEMENTAL ANALYSIS OF CANADIAN VEHICLE CATALYSTS

Number	Vehicle	MY	Mileage	Mn	Pb	S	P	Zn	B.E.T. Area, m_2/g
BK1	Taurus	88	35,733	1.22	.20	.06	.13	.15	19.1
BK2	Sable	89	28,840	0.99	.14	0	.13	.08	19.0
BK3	Sable	88	44,235	0.97	.18	.02	.18	.13	19.0
BK4	Taurus	88	41,093	1.10	.08	0	.13	.07	19.0
BK5	Sable	88	21,500	0.95	.04	.04	.10	.05	14.3
BK6	Taurus	87	48,174	1.74	.13	.07	.12	.09	18.0
BK7A*	Sable	88	62,224	2.07	.18	0	.21	.21	19.7
BK7B*	Sable	88	62,224	3.23	.16	0	.26	.30	12.0
BK8	Taurus	87	53,354	1.27	.22	.06	.16	.11	17.0
BK9	Sable	88	27,416	0.98	.12	0	.21	.15	19.0
BK10	Taurus	88	39,662	0.79	.13	.13	.08	.09	19.3

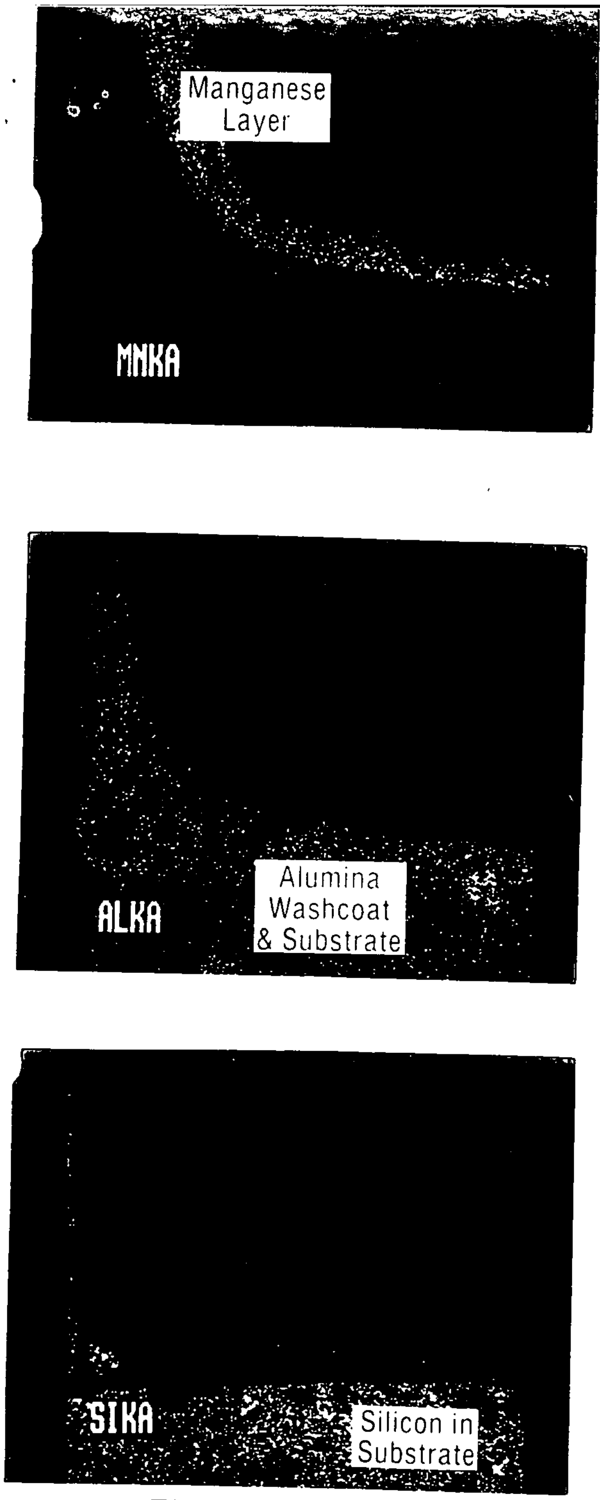
*7A and 7B refer to driver side and passenger side catalysts, respectively on 3.8L catalysts engine system.

Scanning electron microscopy and electron microprobe analysis were used to identify and more precisely measure the thickness of the Mn layer. Shown in Figure 2 are typical secondary electron images and elemental maps of two of the samples. Using these elemental maps one can measure the thickness in the filet area to be 60 microns as compared to the washcoat of approximately 30 microns. Exact measurements of the thickness using electron microprobe linear transverse spectrum analysis (elemental line scans) indicate that the thickness may vary from a low of 17 microns on a rib areas to a high of 81 microns in the filet area of the monolith. These electron microprobe line scans are shown in appendices 6 and 7 for samples BK6 (48,174 miles) and BK7 (62,224 miles).

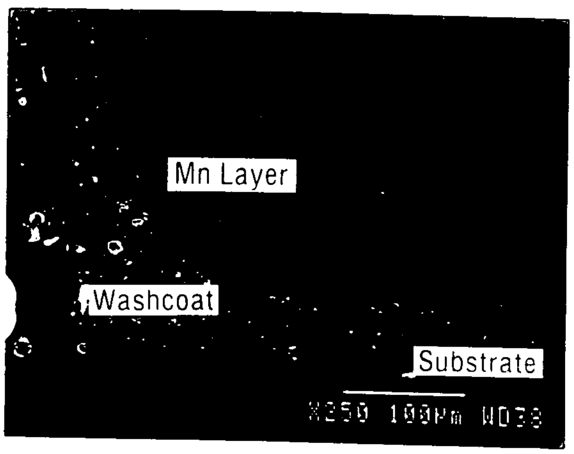
Average B.E.T. surface areas range between 12.0 and 19.0 m^2/g for the catalysts examined in this evaluation (Table 2). The B.E.T. values for inlet, middle, and outlet samples are also given in appendices A-J of this report. This data confirms visual observations that the catalysts were not exposed to abnormally high operating temperatures and were not thermally stressed prior to removal from the vehicle. Fresh catalysts generally exhibit B.E.T. values of approximately 25 m^2/g whereas an aged catalyst could have a B.E.T value as low as 5 m^2/g and still retain considerable catalytic activity. The lowest value of 12 m^2/g was observed for the 62,224 miles vehicle and this is not considered to be outside of the normal range for vehicles with this mileage accumulation.

Laboratory measurements of conversion efficiencies and lightoff characteristics were obtained for each of the catalysts using synthetic exhaust gas mixtures. The steady state and light-off curves for each individual sample are given in appendices A-J. The HC efficiencies are summarized in figures 3-5. In these figures percent HC efficiency is plotted against R values (redox ratio). The redox ratio, is a measure of the exhaust stoichiometry and is related to the A/F ratio. An $R > 1$ indicates a net excess of reducing species (CO and HC) and $R < 1$ indicates a net excess of oxidizing species (NO and O_2). Included in this summary for comparison is data from a catalyst obtained from a <u>non-MMT fueled</u> vehicle of comparable mileage, model and year. The data show that HC efficiency is significantly reduced in those catalysts that have been exposed to the fuel additive MMT when compared to those catalysts from a vehicle operated without MMT in the fuel. Figure 6 shows similar HC efficiency curves for outlet portions from the catalysts used in this study. In those cases where the Mn concentration is low (approximately 0.3 wt%), the efficiencies compare favorably with the catalyst from the non-MMT fueled vehicle. In the case of the high mileage MMT fueled vehicle (62,224 miles) which has approximately 0.9 wt% Mn, and the decrease in HC efficiency is significant at $R = 1$, indicates that Mn has a pronounced effect on catalyst activity at concentrations as low as 1 wt%.

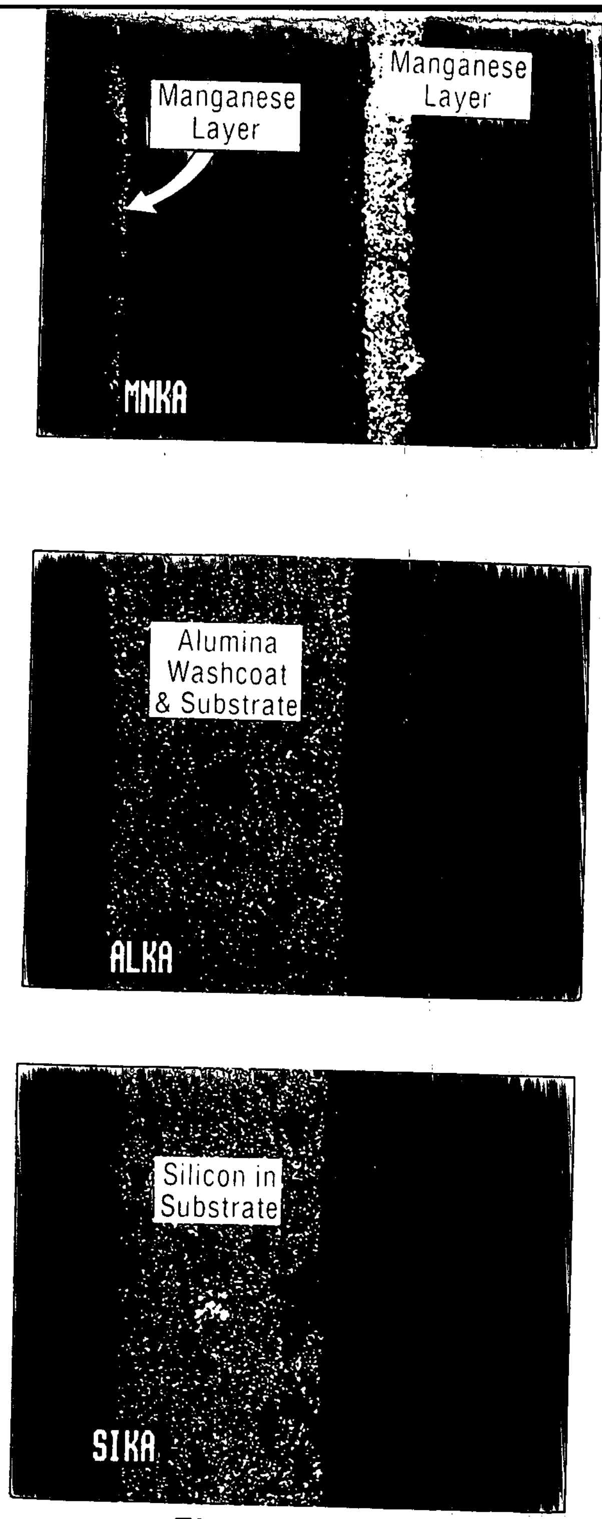
The EGO sensors taken from each of the vehicles were submitted to ELD (Electronics Division's sensors group) and to the Robert Bosch Company for more detailed analysis. The results show that each was coated with a layer of Mn and that each was functioning. However, the EGO from vehicles BK7 (62,224 miles) and BK9 (27,416 miles) exhibited some abnormal behavior but were still classified as being within specifications for functioning EGOs.



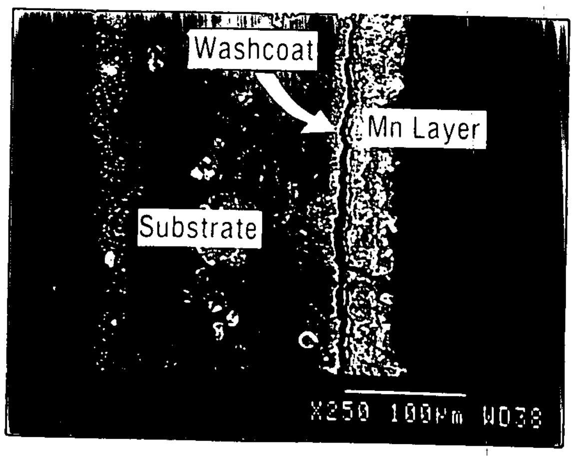
Elemental Maps



Secondary Electron Image Of Fillet Area



Elemental Maps



Secondry Electron Image Of Rib Area

Figure 2- Secondary Electron Elemental Mapping of Sample BK6 & 7a

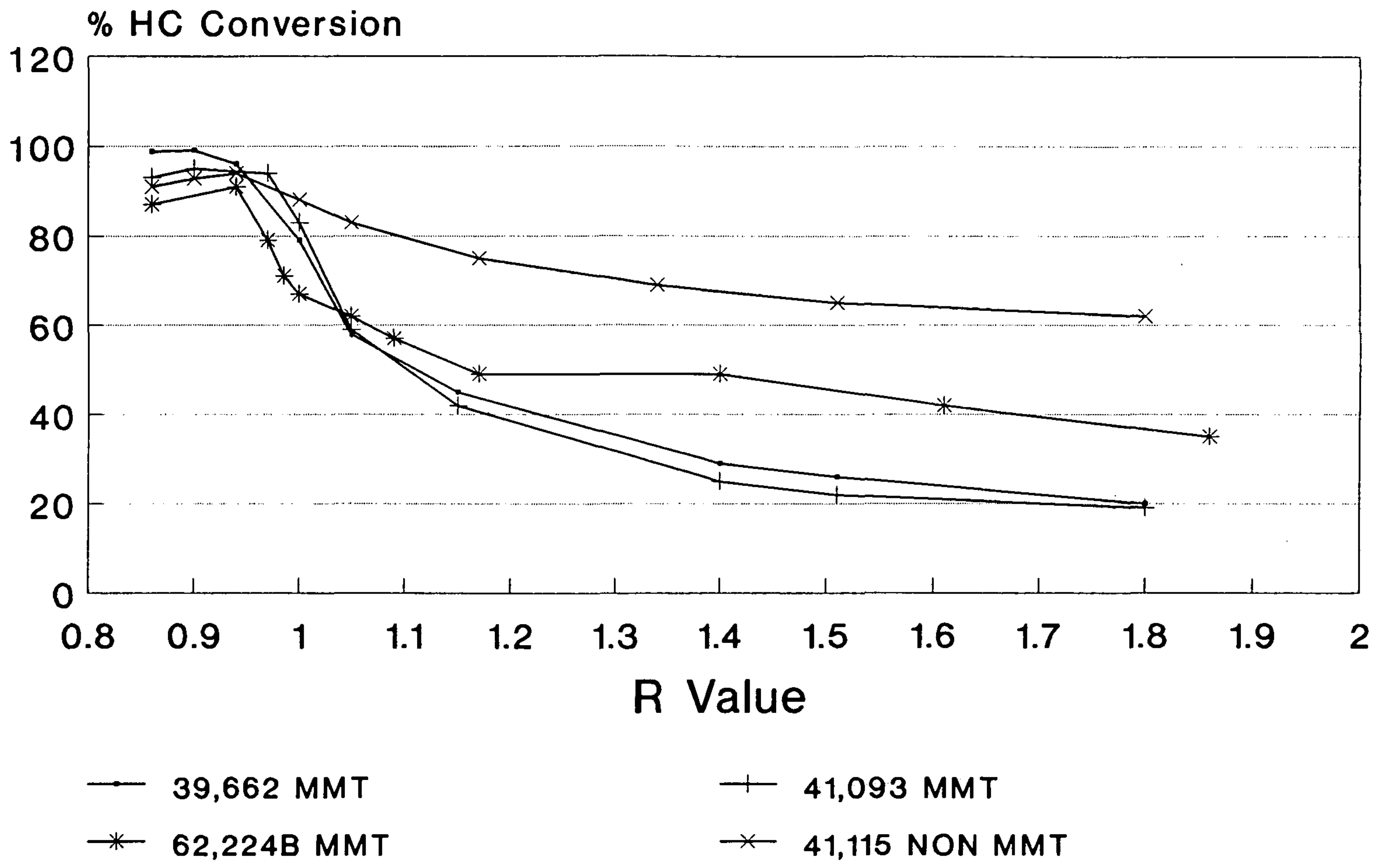


Figure 3- HC Efficiencies of Inlet Samples versus Redox Ratio

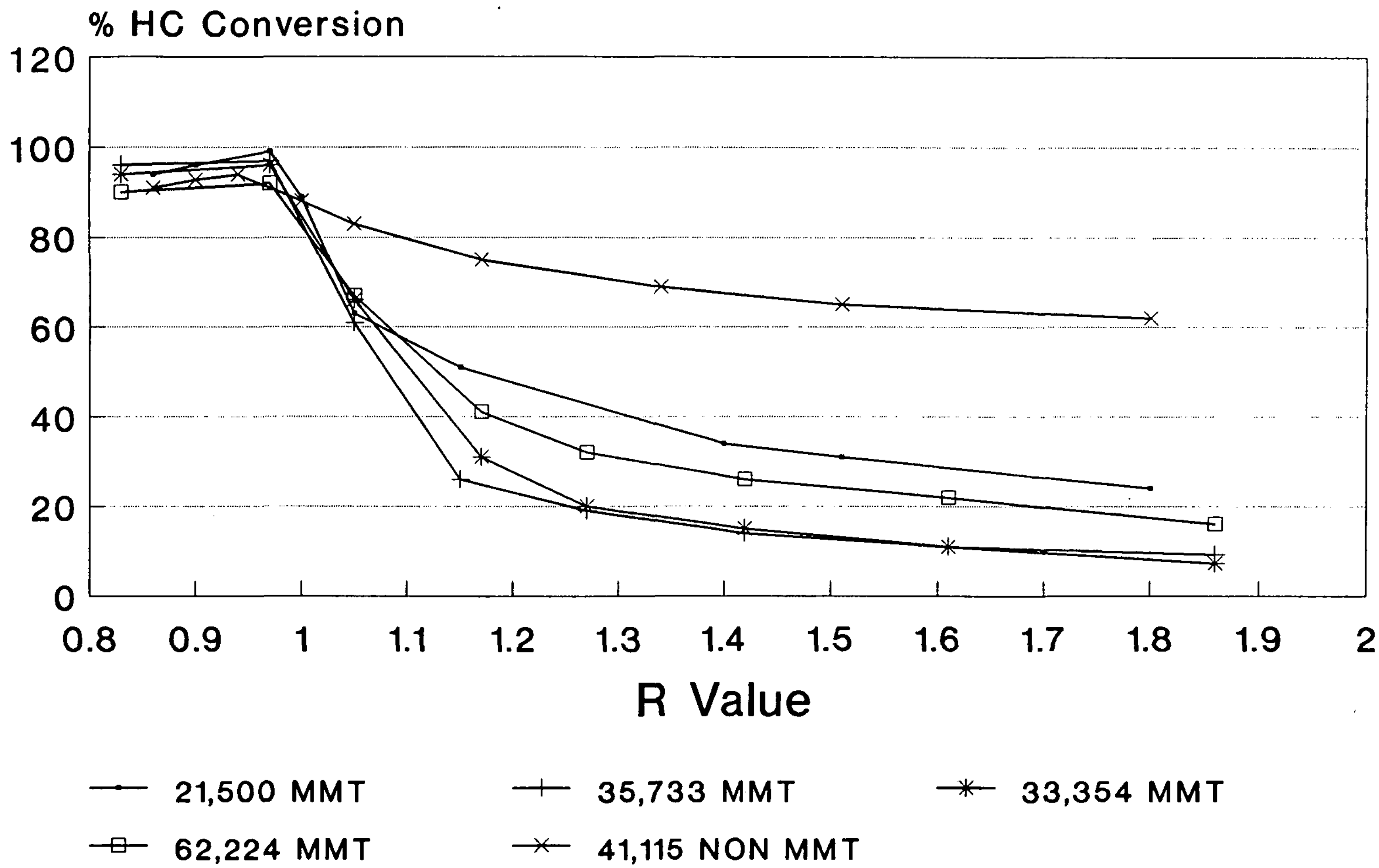


Figure 4- HC Efficiencies of Inlet Samples versus Redox Ratio

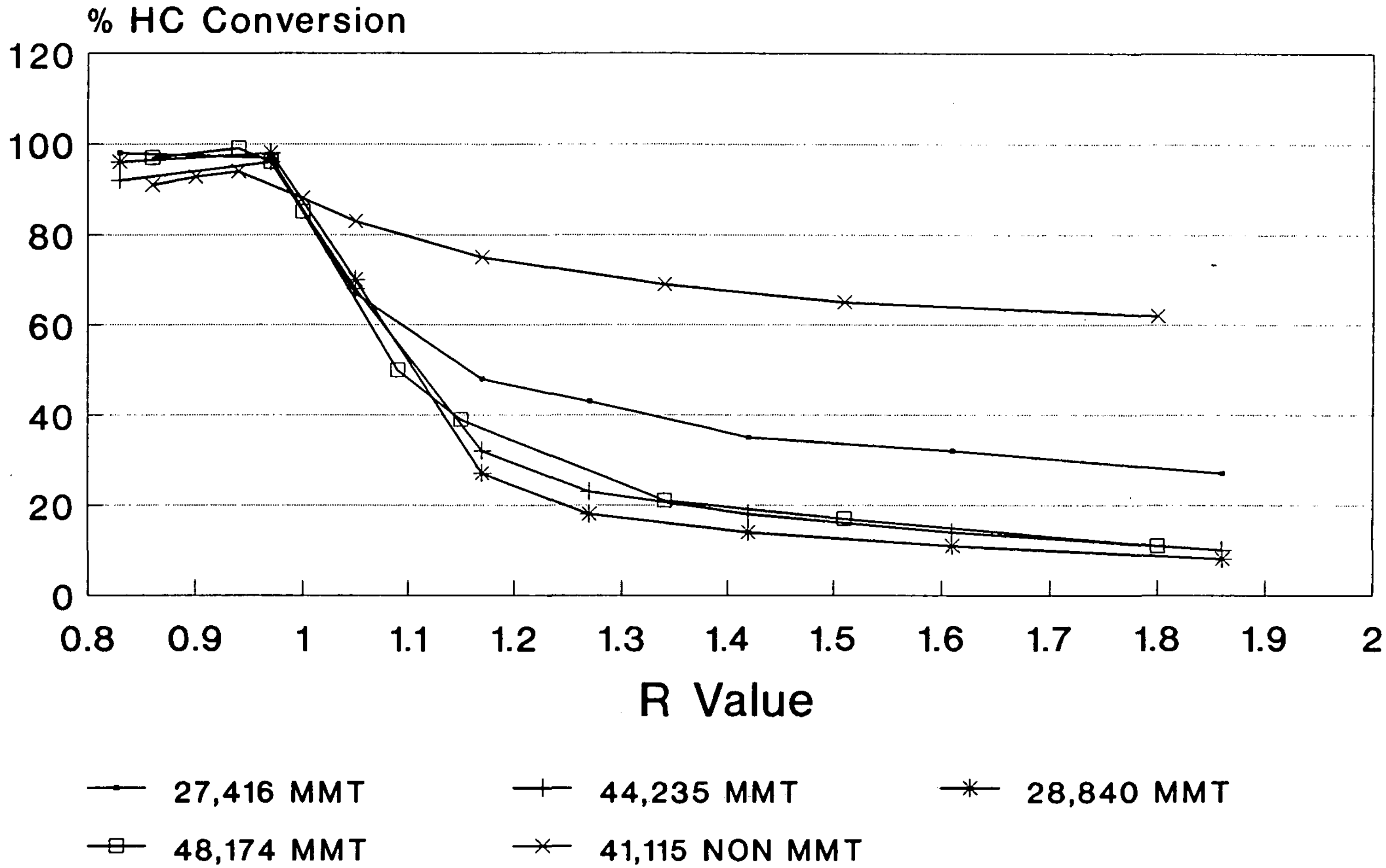
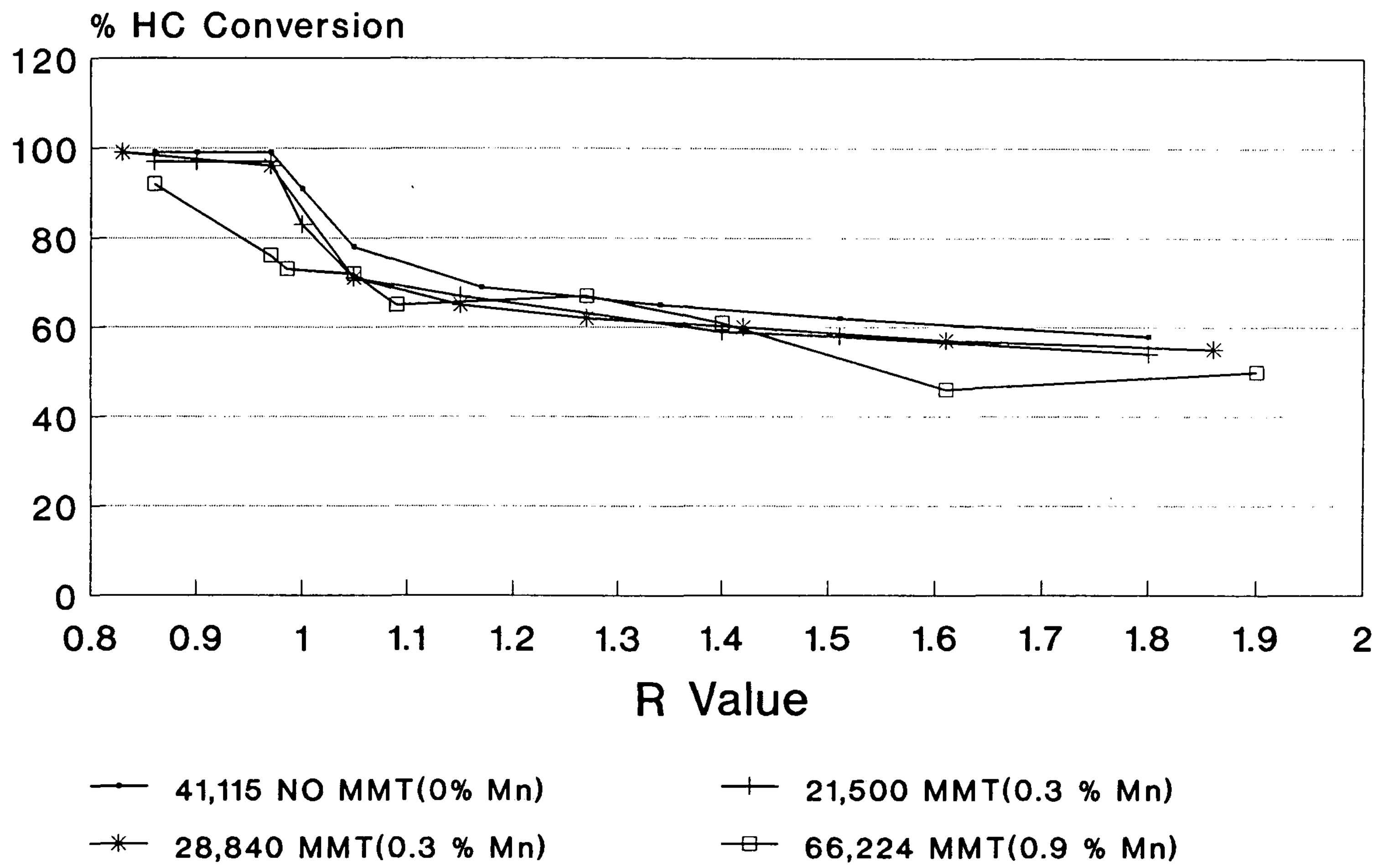


Figure 5- HC Efficiencies of Inlet Samples versus Redox Ratio



Samples from Outlet Portion

Figure 6- HC Efficiencies of Outlet Samples versus Redox Ratio

Summary

In summary, the efficiency of catalyst exposed to the fuel additive MMT (1/16 g Mn/gal) is significantly reduced. The data obtained from this set of catalysts taken from vehicles which were employee driven and had experienced no operational problems confirms those conclusions drawn from earlier data that the combustion product of MMT, Mn_3O_4, does affect significantly the efficiency of the catalyst. This data shows conclusively that the Mn_3O_4 layer which begins to build even in low mileage vehicles adversely affects the ability of the catalyst to convert HC and NO_x in a synthetic exhaust stream. The mechanism for this reduced efficiency is probably increased mass transfer resistance caused by the layer of Mn_3O_4 covering the washcoat. In this mechanism, the exhaust gases must penetrate a thick layer of Mn_3O_4 before they can reach the catalytically active sites on the washcoat. Consequently, this rate inhibiting step results in the reduced catalytic activity observed in this series of samples.

Concur: H. S. Gandhi

R. G. Hurley

<u>Contributors to the data in this report included</u>: L. A. Hansen, D. Lewis, W. L. H. Watkins, C. Marry from the Chemical Engineering Department-Research; F. Kunz, R. Belitz, K. Plummer, R. Warsinski, F. Alberts from the Analytical Sciences Department-Research; and G. Beaudoin from ELD.

Appendix A

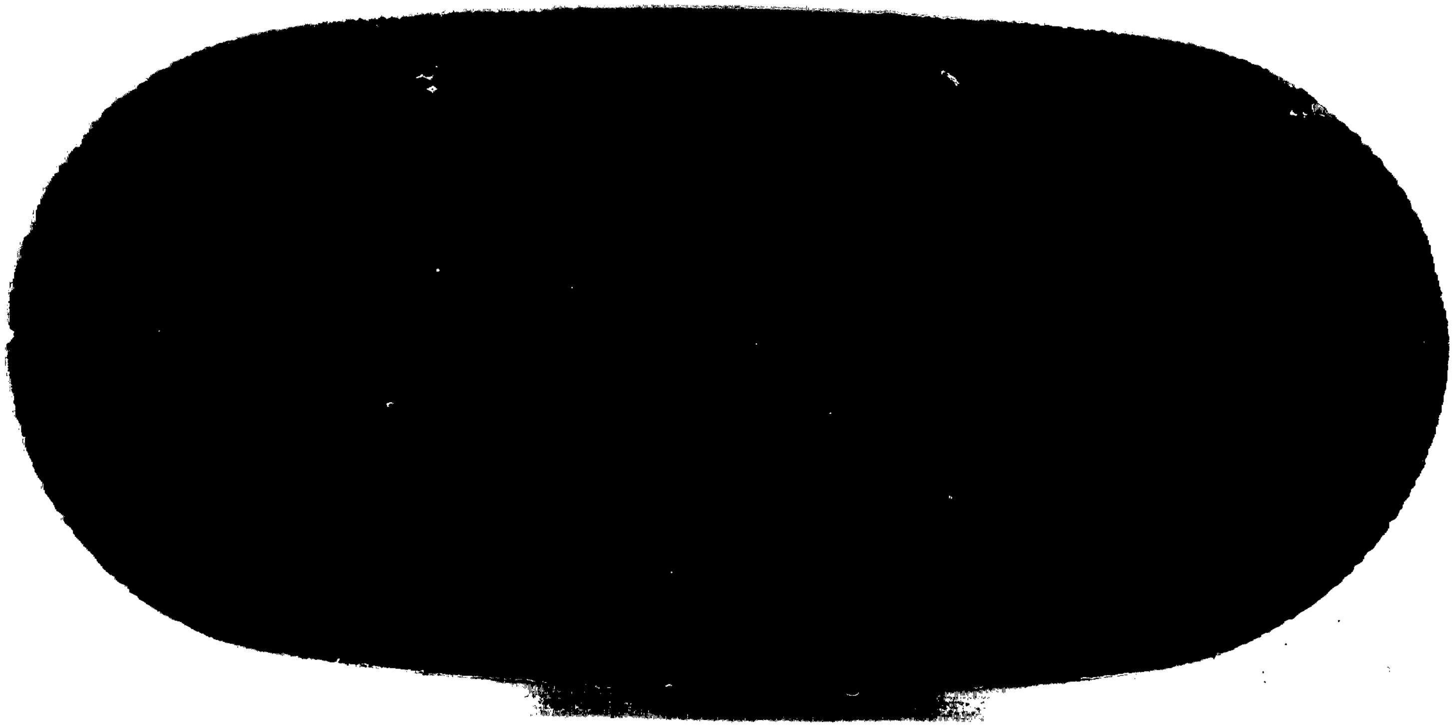
1988 3.0L Taurus

35,733 Miles

X-RAY FLUORESCENCE ANALYSIS OF MMT CATALYSTS

VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) CATALYTIC COMPONENTS PT	RH	PD	NI	CE	BA	LA	FE	g/ft^3	Pt/Pd/Rh
1989 3.0L Taurus		**35,733 Miles**									
MMT-BK1I	20.6	.1979	.0411	.0000	.7654	6.1937	.8242	.2404	.3553	34.9	4.8/0/1.0
MMT-BK1M	18.9	.1705	.0355	.0000	.6886	6.2911	.7281	.2422	.3237	30.1	4.8/0/1.0
MMT-BK1O	17.8	.1659	.0341	.0000	.6491	6.1441	.6509	.2391	.3399	29.2	4.9/0/1.0
									Average:	31.4	4.8/0/1.0

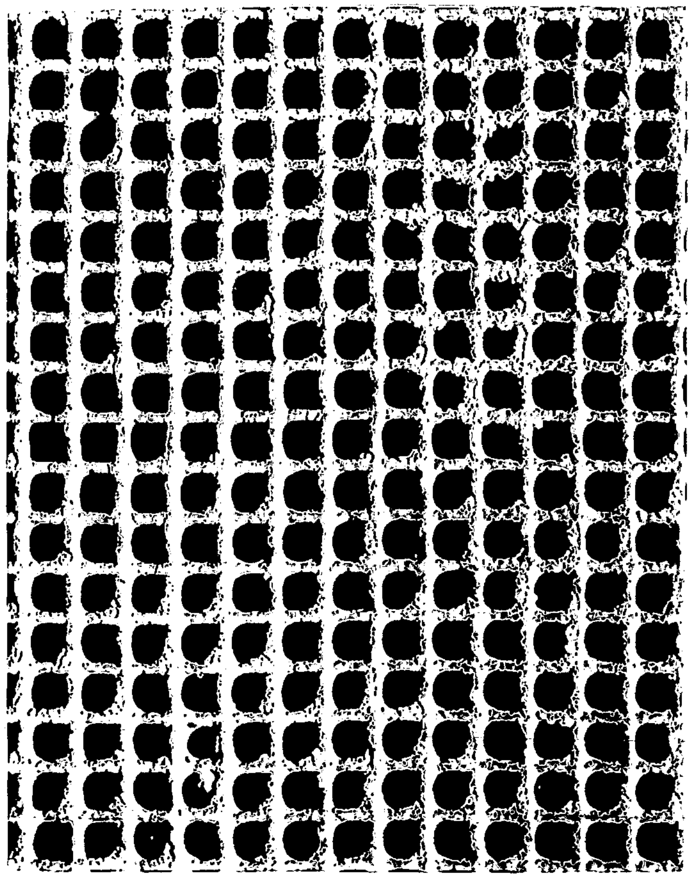
VEHICLE CATALYST	CONTAMINATES PB	S	P	ZN	MN	CA	CL	CU
MMT-BK1I	.2031	.0642	.1269	.1534	1.2169	.0604	.0000	.0254
MMT-BK1M	.0722	.0000	.0749	.0447	.7475	.0195	.0000	.0227
MMT-BK1O	.0458	.0049	.0648	.0326	.6938	.0327	.0000	.0202



1988 TAURUS
3.0L ENGINE
35,733 MILES

1988 3.0L Taurus- 35,733 Miles

Inlet



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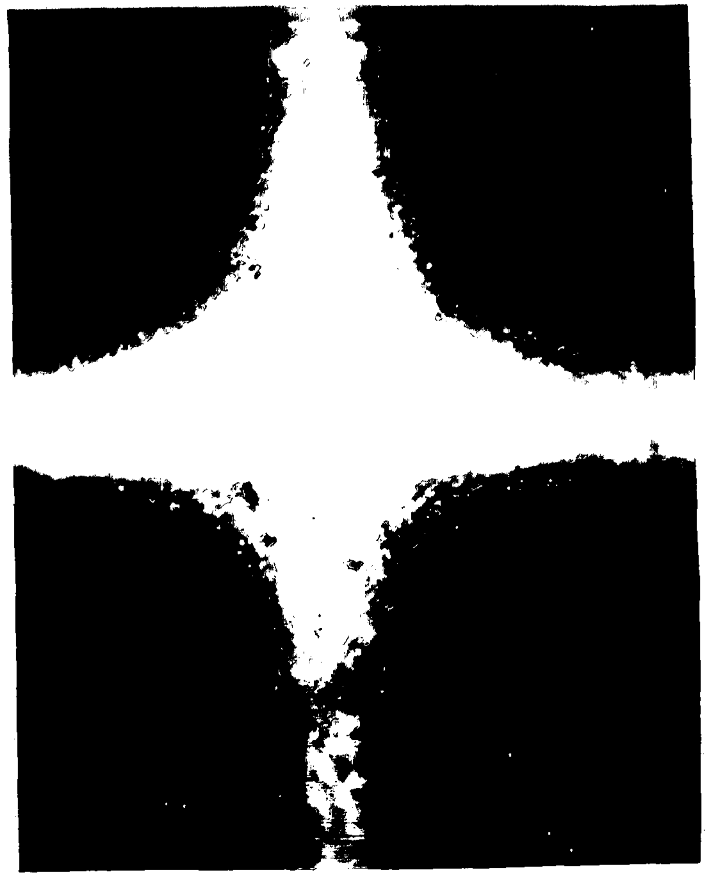
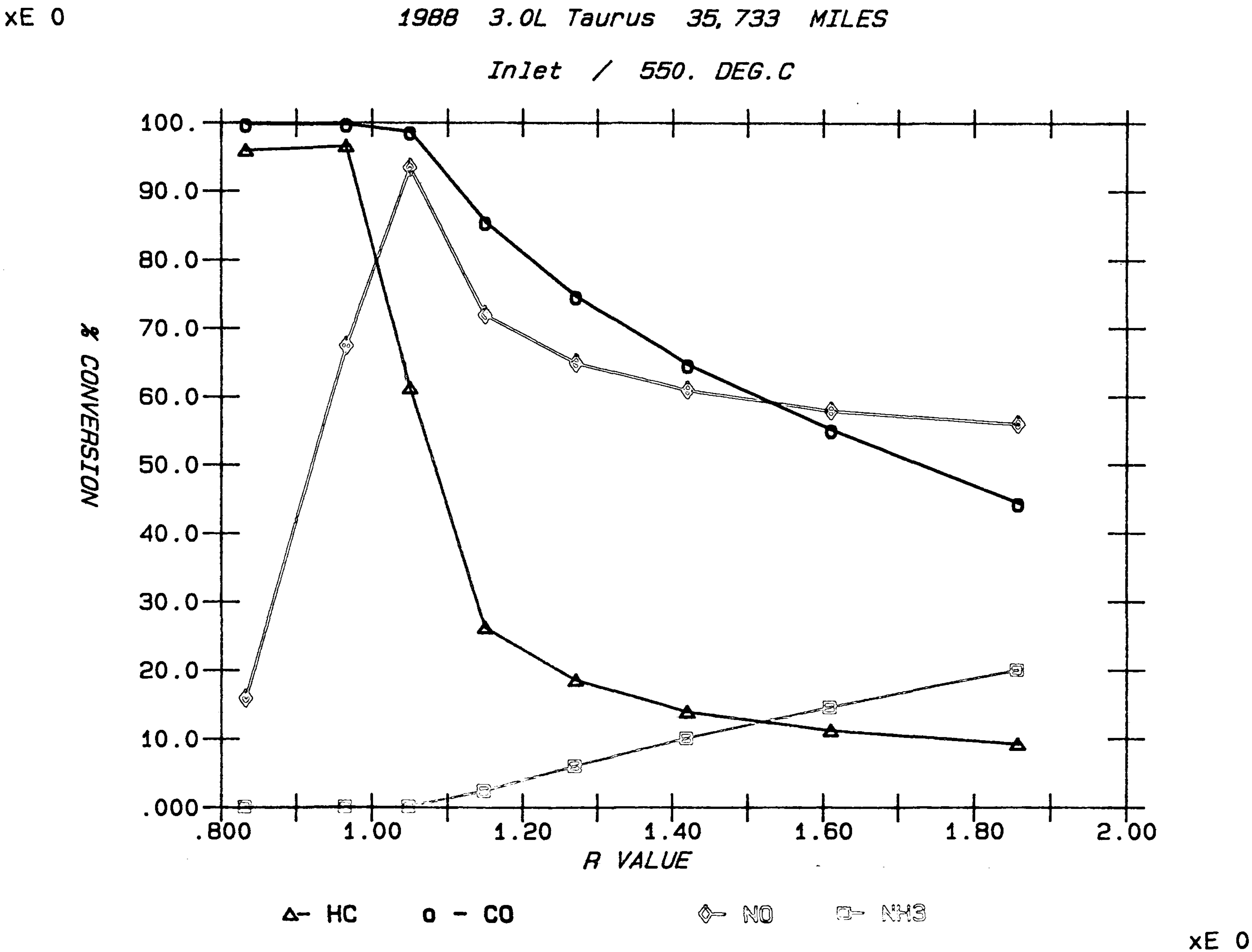


80X

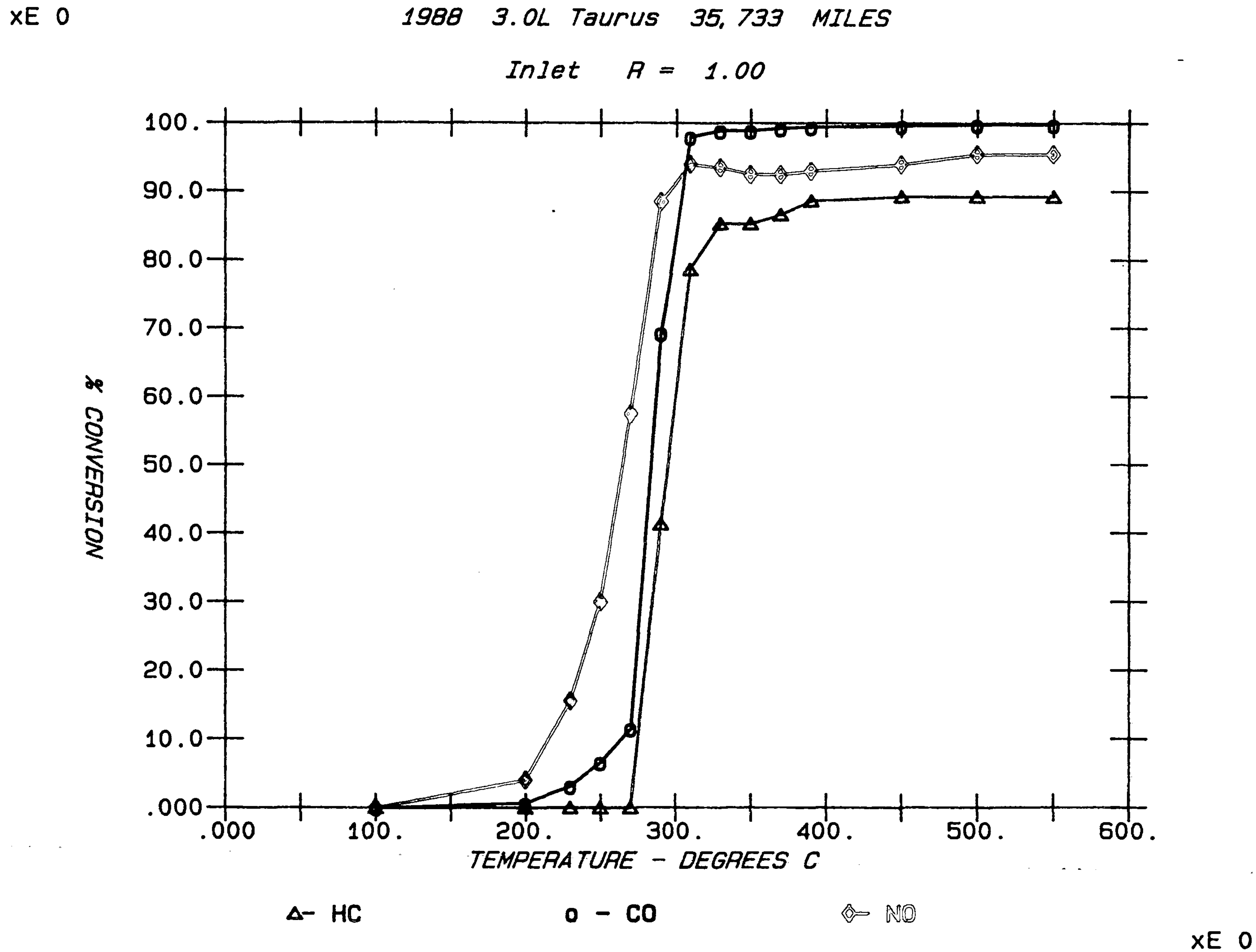
1988 3.0L Taurus 35, 733 MILES

Inlet / 550. DEG.C



1988 3.0L Taurus 35,733 MILES

Inlet R = 1.00



Appendix B

1989 3.0L Sable
28,840 Miles

X-RAY FLUORESCENCE ANALYSIS OF MMT CATALYSTS

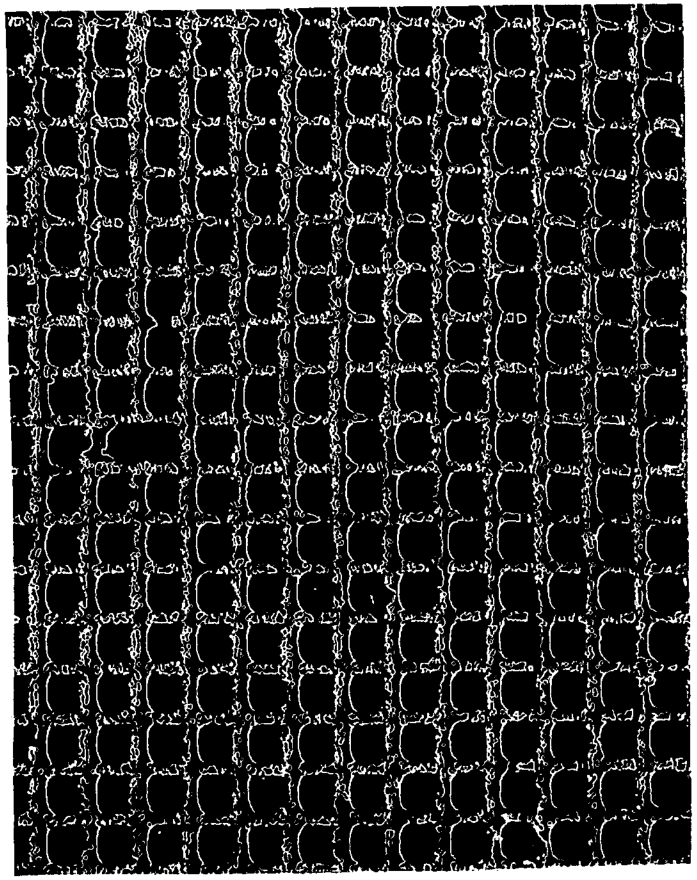
VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) CATALYTIC COMPONENTS PT	RH	PD	NI	CE	BA	LA	FE	g/ft^3	Pt/Pd/Rh
1989 3.0L Sable		**28,840 Miles**									
MMT-BK2I	19.5	.2058	.0438	.0000	.7243	5.0654	.6672	.1975	.3525	36.4	4.7/0/1.0
MMT-BK2M	19.9	.1861	.0408	.0000	.7135	5.3654	.6184	.2052	.3491	33.1	4.6/0/1.0
MMT-BK2O	17.4	.1779	.0372	.0000	.6304	5.1285	.5896	.1987	.3523	31.4	4.8/0/1.0
									Average:	33.6	4.7/0/1.0

VEHICLE CATALYST	CONTAMINATES PB	S	P	ZN	MN	CA	CL	CU
MMT-BK2I	.1393	.0000	.1284	.0756	.9894	.0374	.0000	.0248
MMT-BK2M	.0369	.0000	.0499	.0114	.4615	.0165	.0000	.0198
MMT-BK2O	.0219	.0000	.0353	.0096	.3313	.0152	.0000	.0222

1989 SABLE
3.0L ENGINE
28,840 MILES

1989 3.0L Sable- 28,840 Miles

Inlet



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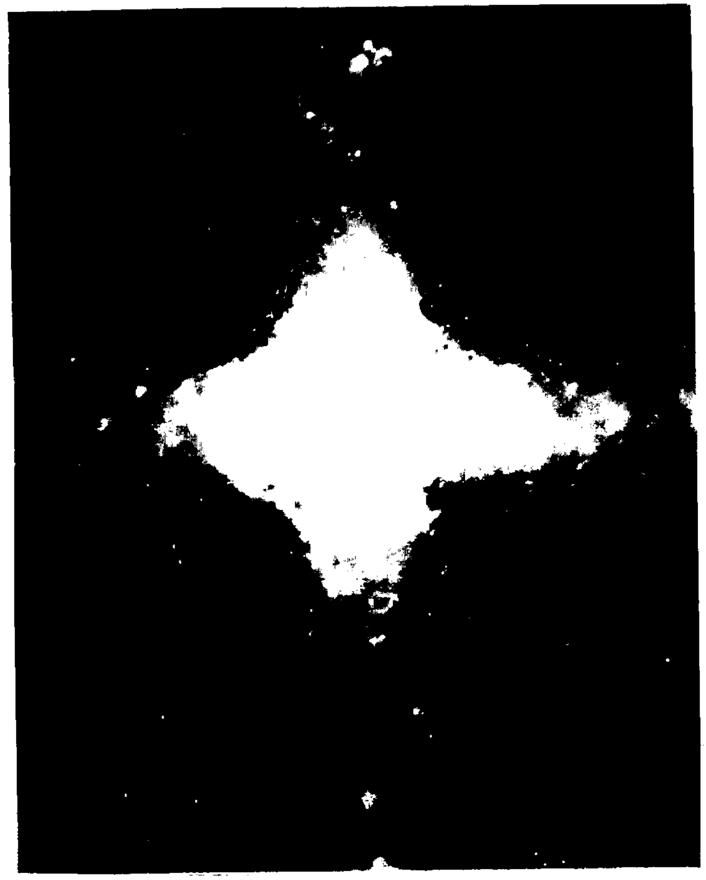

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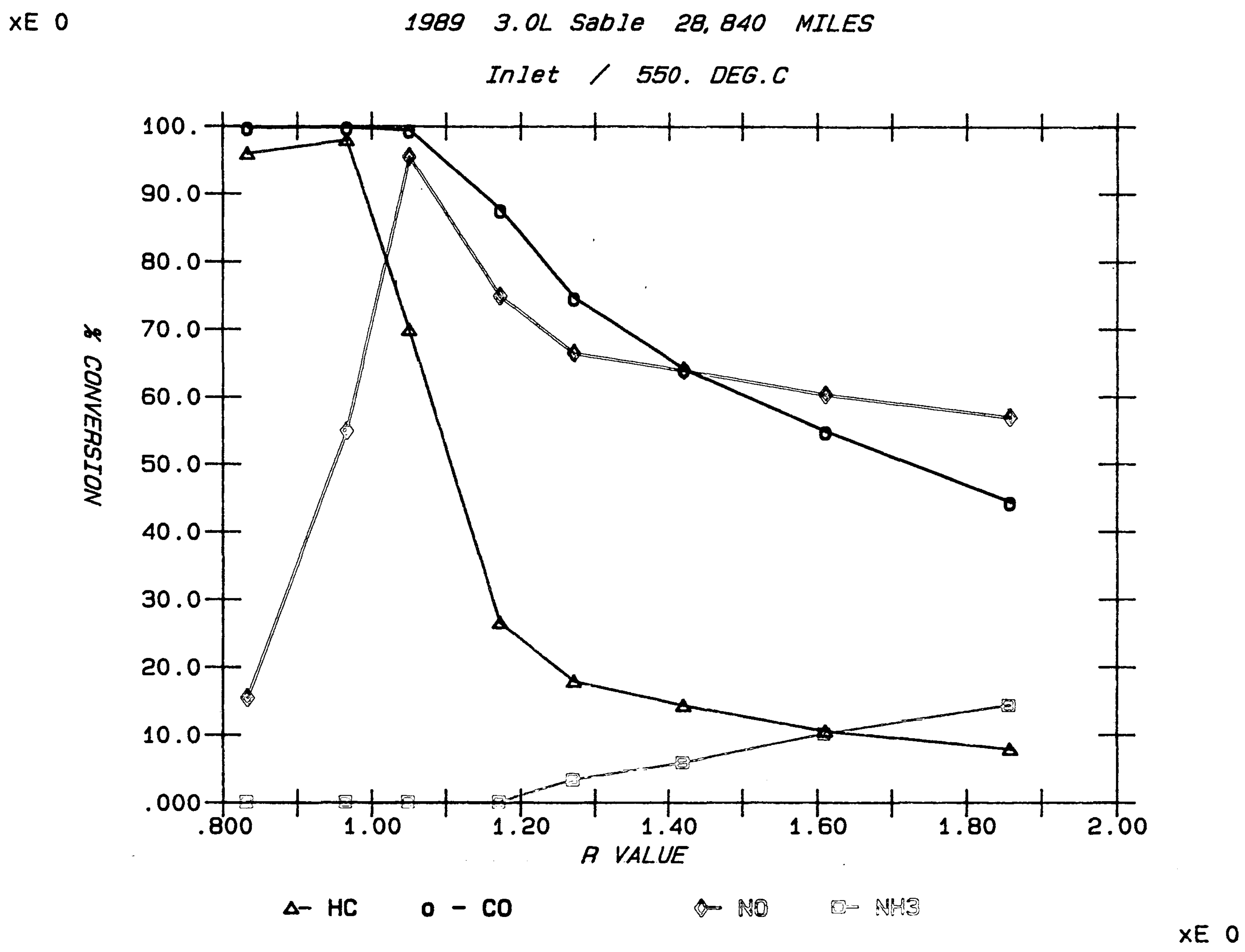
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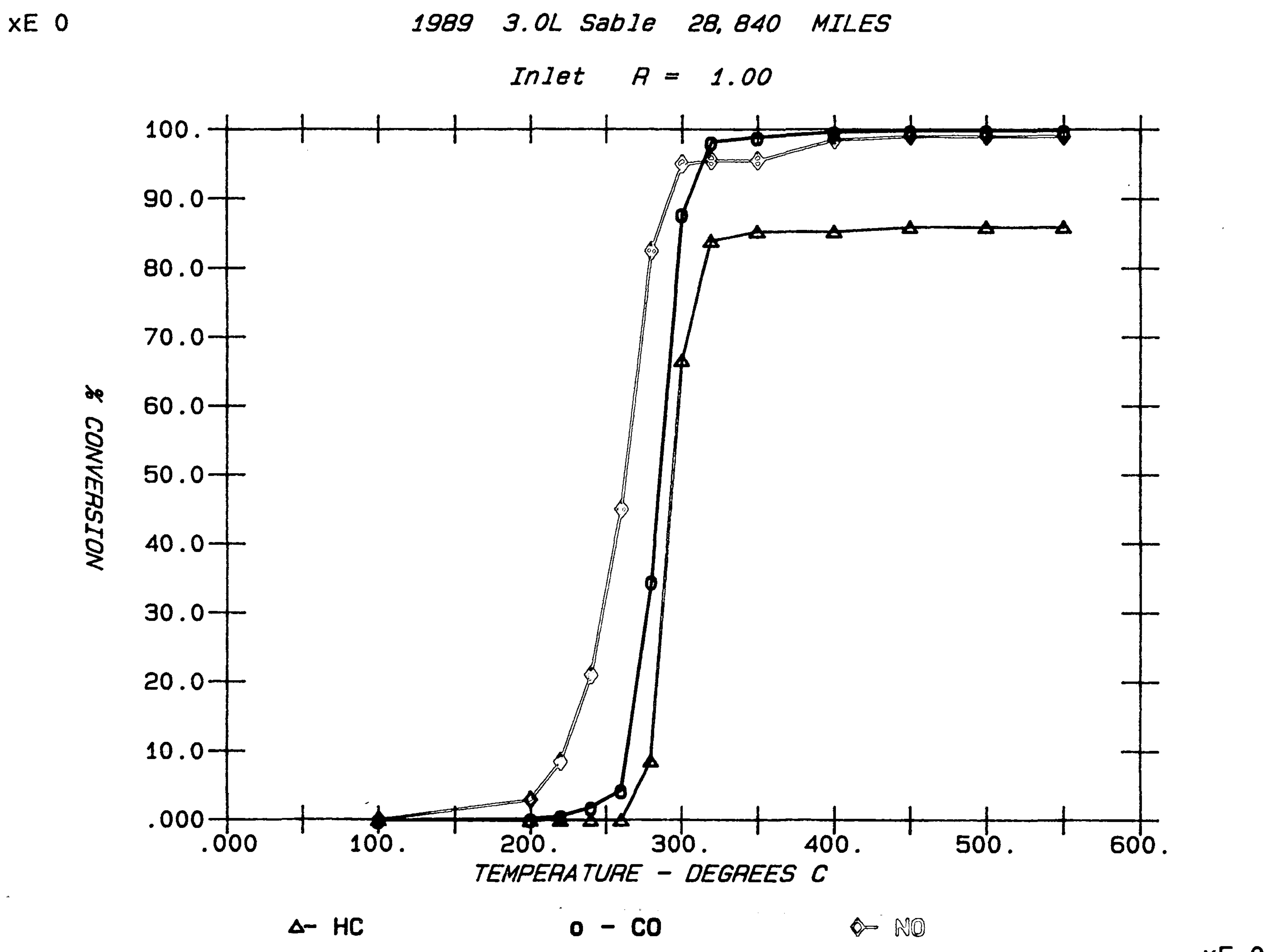
1989 3.0L Sable 28,840 MILES
Inlet / 550. DEG.C
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
Δ- HC
o - CO
◇- NO
□- NH3
xE 0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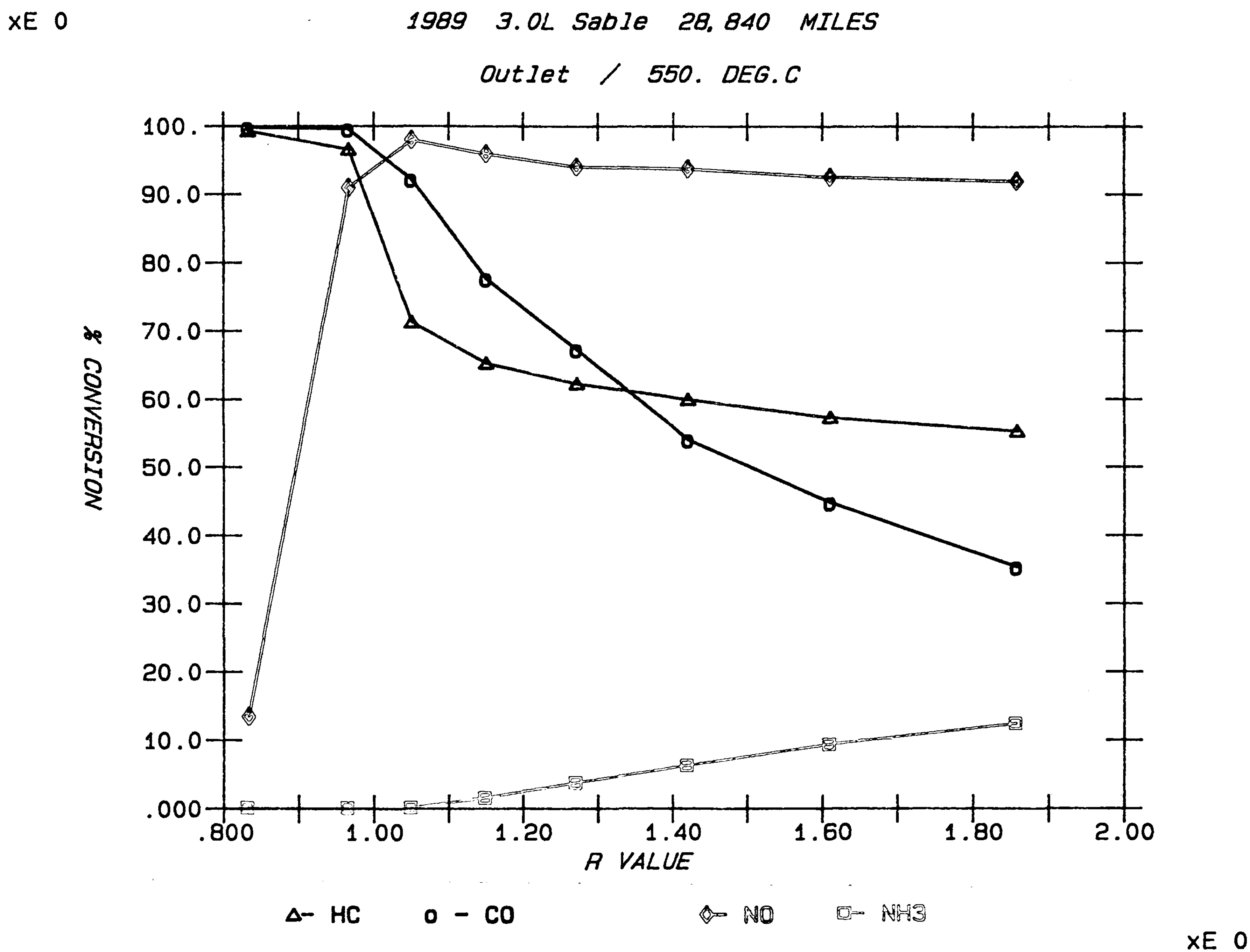
1989 3.0L Sable 28,840 MILES
Inlet R = 1.00
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
Δ- HC
o - CO
◇- NO
xE 0



xE 0
1989 3.0L Sable 28,840 MILES
Outlet / 550. DEG.C
% CONVERSION
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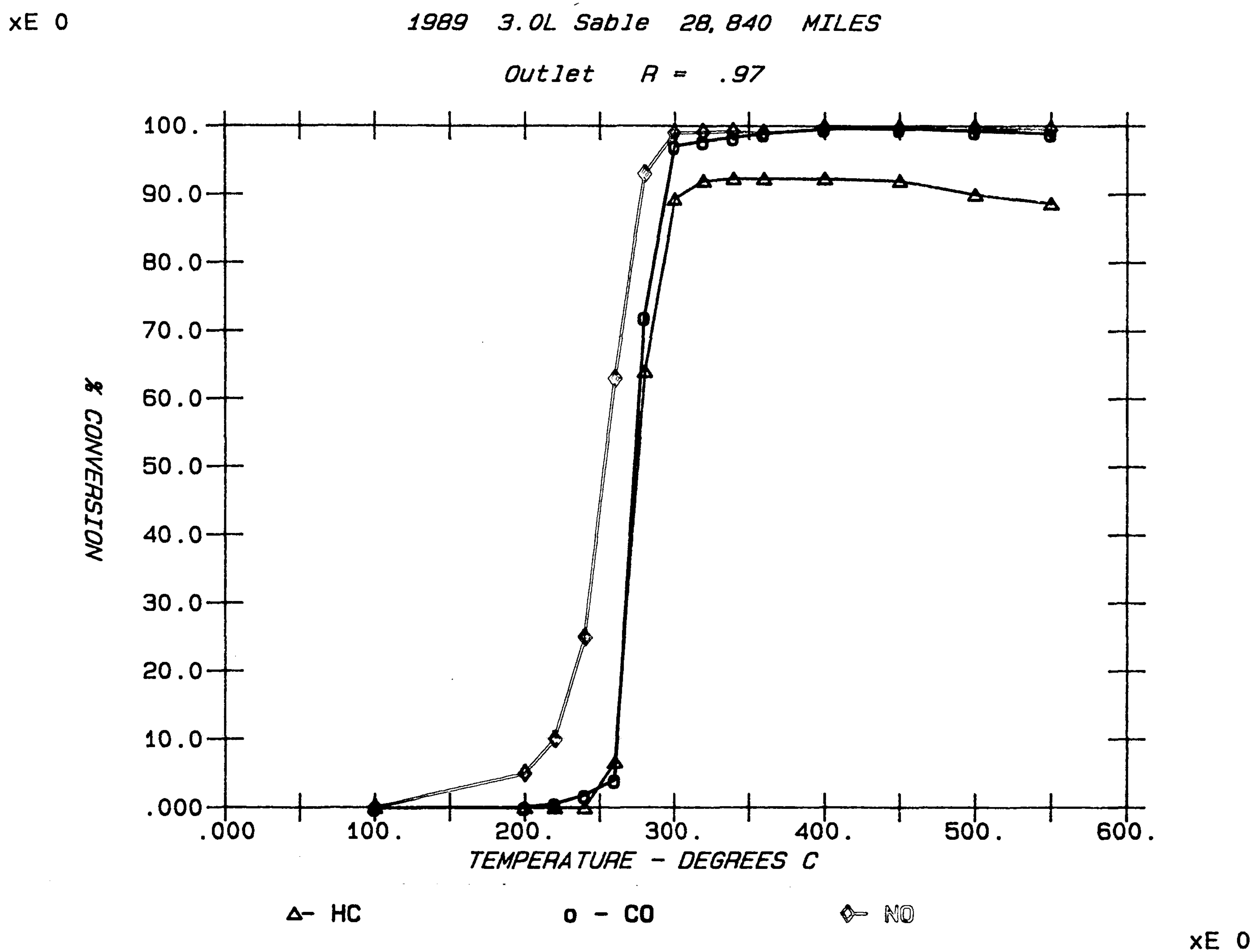
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
HC
CO
NO
NH3
xE 0



xE 0
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Outlet R = .97
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
Δ- HC
o - CO
◇- NO
xE 0

35

Appendix C

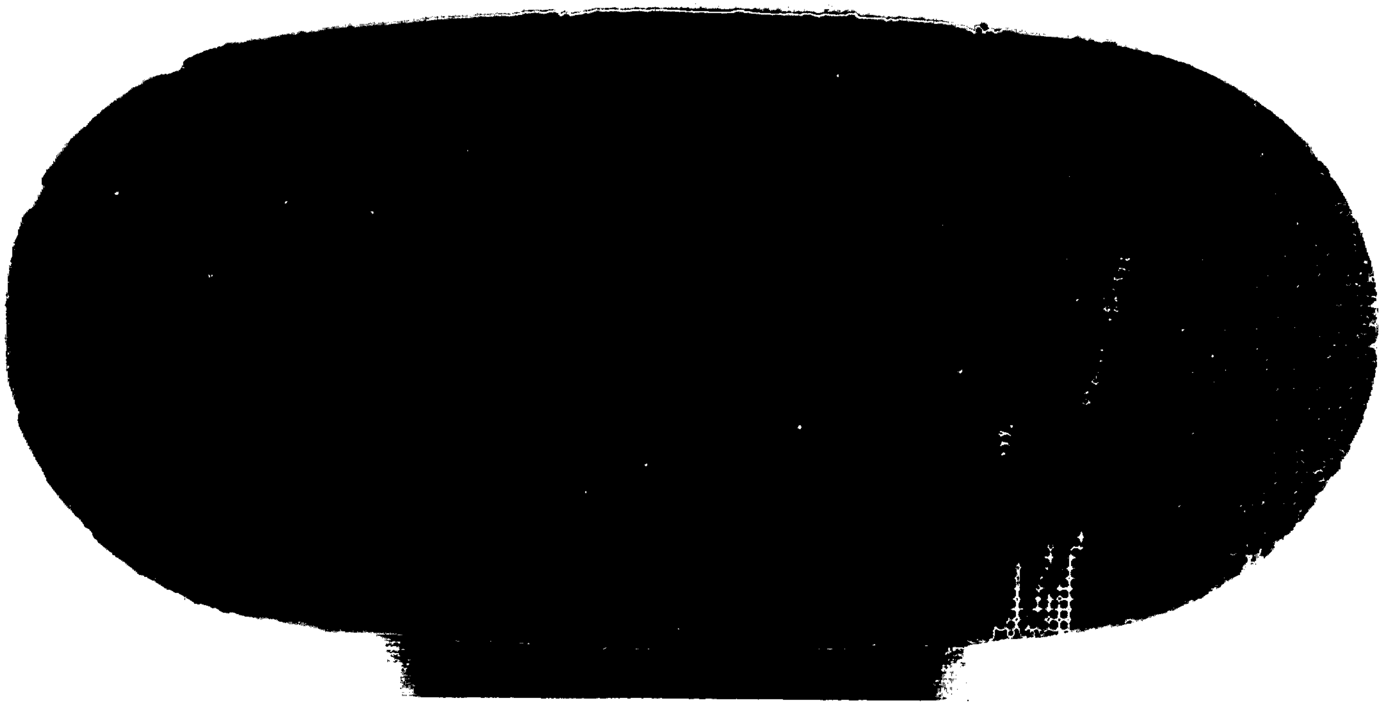
1988 3.0L Sable

44,235 Miles

X-RAY FLUORESCENCE ANALYSIS OF MMT CATALYSTS

VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) CATALYTIC COMPONENTS PT	RH	PD	NI	CE	BA	LA	FE	g/ft^3	Pt/Pd/Rh
1988 3.0L Sable		**44,235 Miles**									
MMT-BK3I	21.2	.1024	.0227	.0000	.7512	6.0490	.6420	.1715	.3933	18.3	4.5/0/1.0
MMT-BK3M	16.6	.1040	.0235	.0000	.7059	5.8953	.6835	.1698	.3740	18.6	4.4/0/1.0
MMT-BK3O	18.5	.0927	.0223	.0000	.6497	5.5785	.6124	.1597	.3846	16.8	4.2/0/1.0
									Average:	17.9	4.4/0/1.0

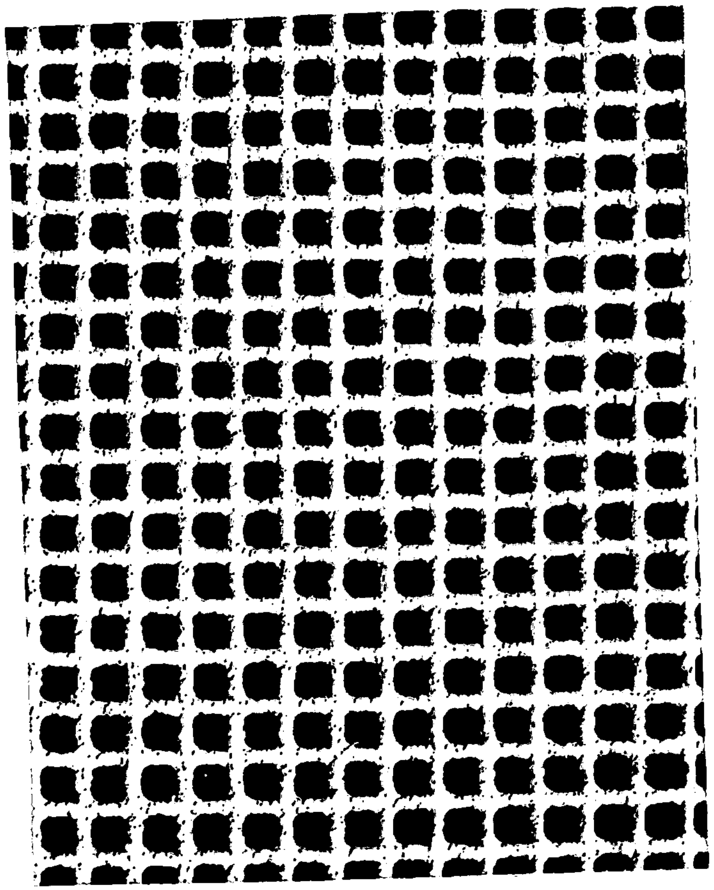
VEHICLE CATALYST	CONTAMINATES PB	S	P	ZN	MN	CA	CL	CU
MMT-BK3I	.1784	.0235	.1782	.1329	.9651	.0449	.0000	.0282
MMT-BK3M	.0626	.0000	.0943	.0349	.6066	.0328	.0000	.0234
MMT-BK3O	.0480	.0000	.0739	.0209	.4640	.0329	.0000	.0239



1988 Sable
3.0L Engine
44,235 Miles

1988 3.0L Sable- 44,235 Miles

Inlet



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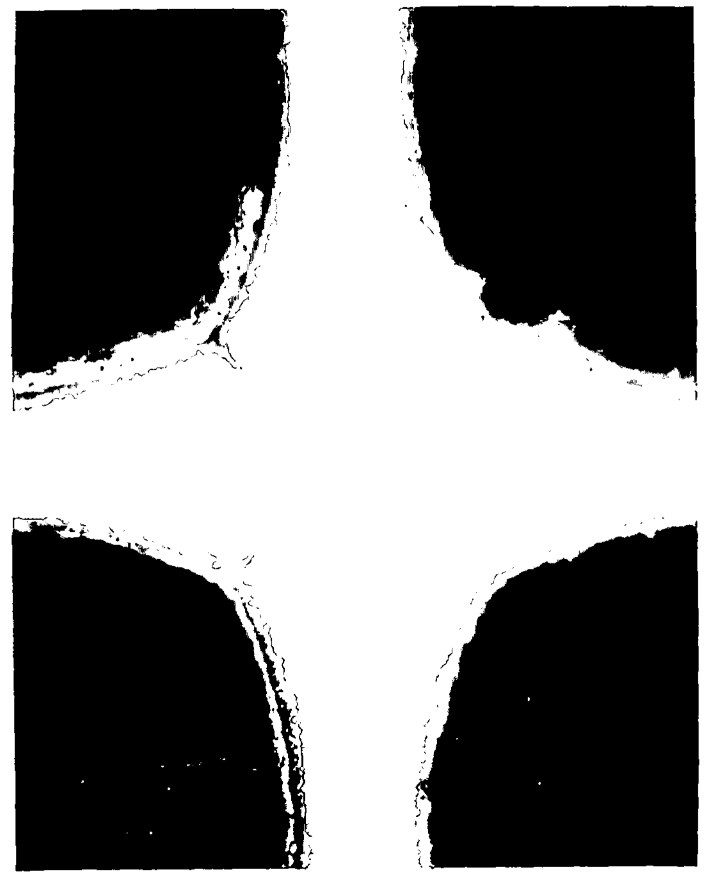

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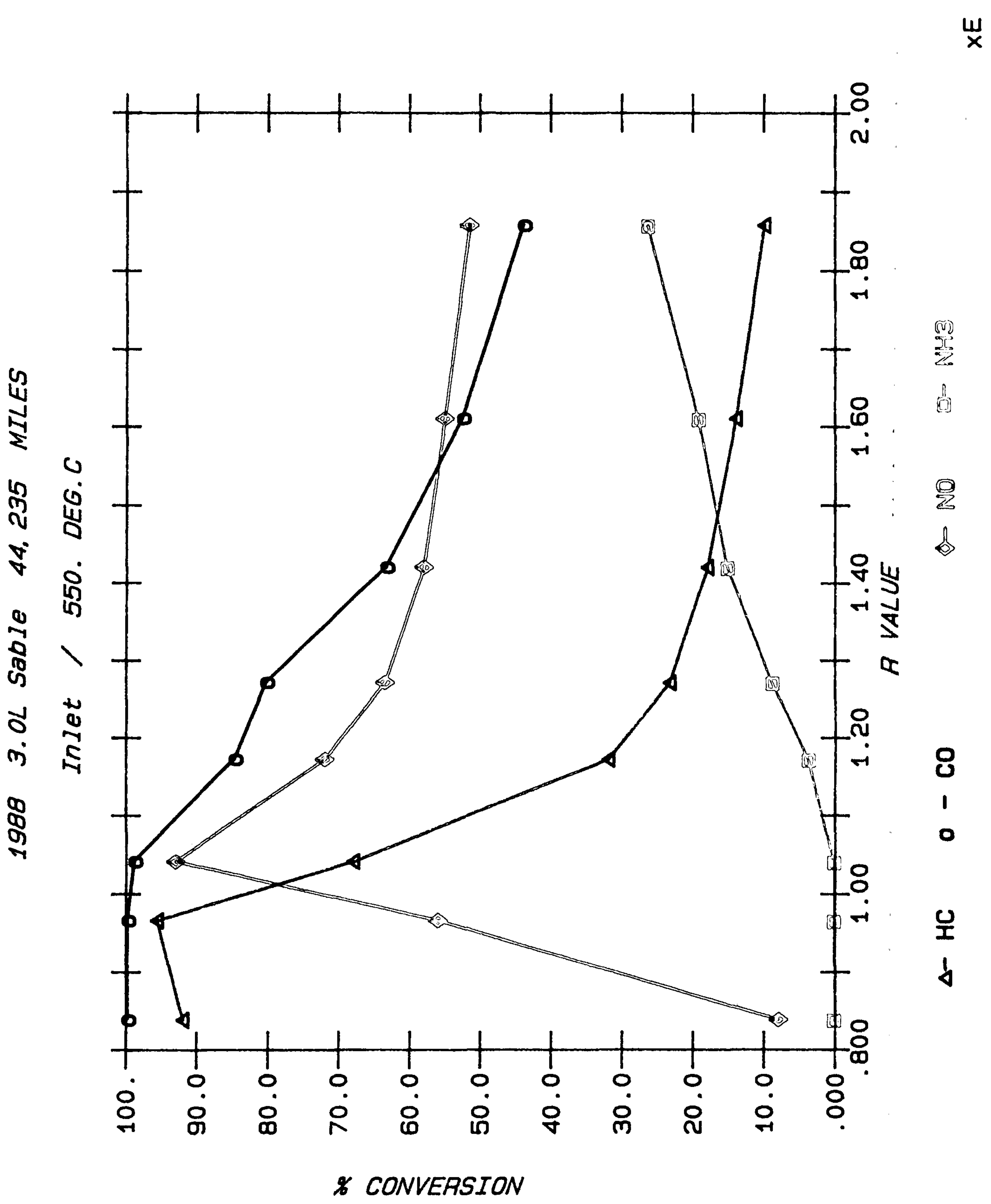
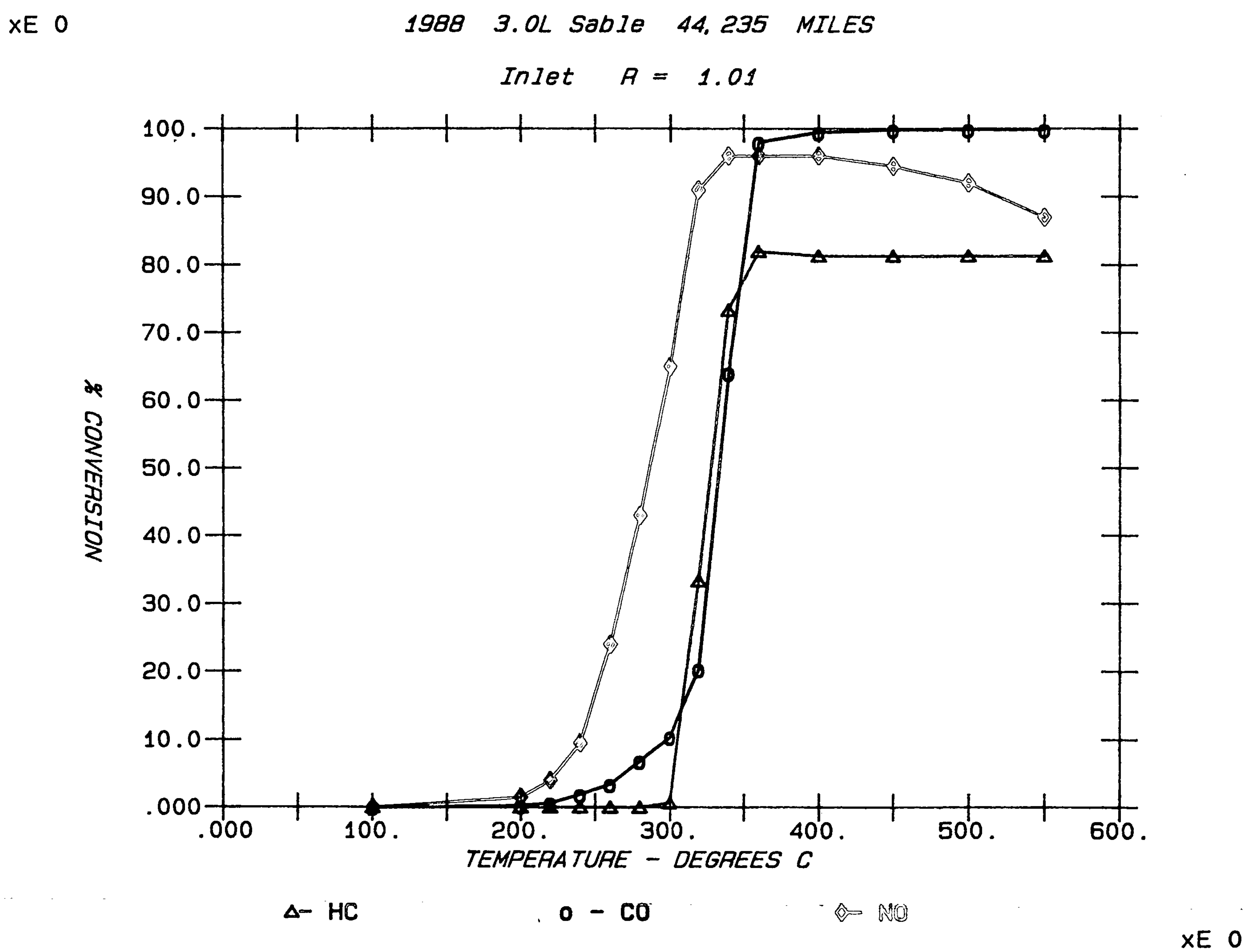

1988 3.0L Sable 44,235 MILES
Inlet / 550. DEG.C
% CONVERSION
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
xE 0
xE 0
HC
o - CO
NO
NH3


1988 3.0L Sable 44,235 MILES
Inlet R = 1.01
xE 0
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
Δ- HC
o - CO
◇- NO
xE 0

Appendix D

1988 3.0L Taurus

41,093 Miles

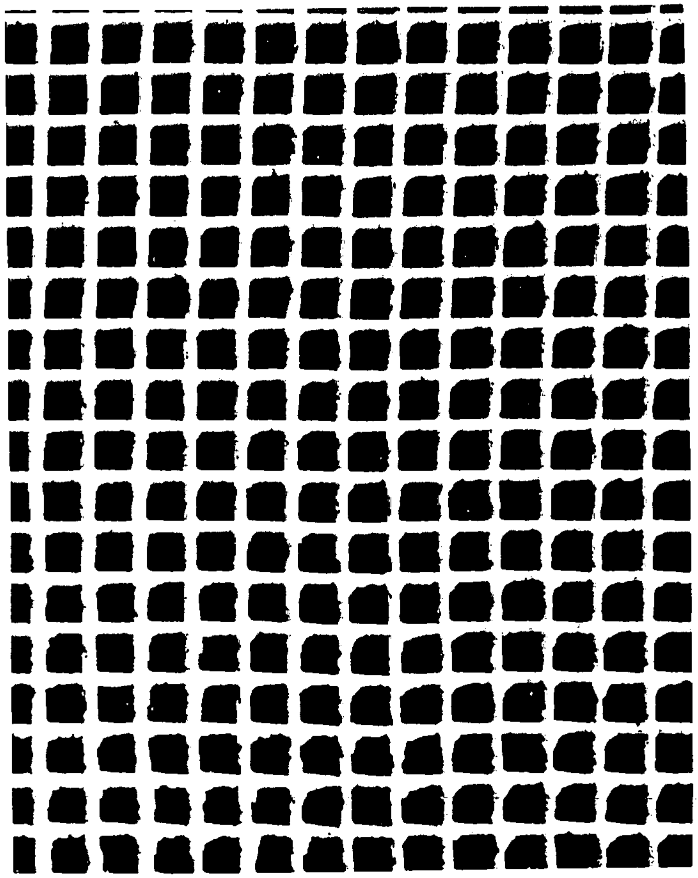
X-RAY FLUORESCENCE ANALYSIS OF MMT CATALYSTS

VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) CATALYTIC COMPONENTS PT	RH	PD	NI	CE	BA	LA	FE	g/ft^3	Pt/Pd/Rh
1988 3.0L Taurus		**41,093 Miles**									
MMT-BK4I	17.8	.1517	.0298	.0000	.6795	6.0095	.5896	.2234	.3625	26.5	5.1/0/1.0
MMT-BK4M	20.6	.1745	.0367	.0000	.6933	6.0214	.6997	.2249	.3584	30.8	4.8/0/1.0
MMT-BK4O	18.6	.1909	.0408	.0000	.6496	5.5291	.7712	.2060	.3794	33.8	4.7/0/1.0
									Average:	30.4	4.8/0/1.0

VEHICLE CATALYST	CONTAMINATES PB	S	P	ZN	MN	CA	CL	CU
MMT-BK4I	.0788	.0000	.1340	.0675	1.0995	.0260	.0000	.0301
MMT-BK4M	.0262	.0000	.0792	.0197	.5962	.0159	.0000	.0234
MMT-BK4O	.0155	.0000	.0565	.0151	.4208	.0170	.0000	.0234

1988 3.0L Taurus- 41,093 Miles

Inlet



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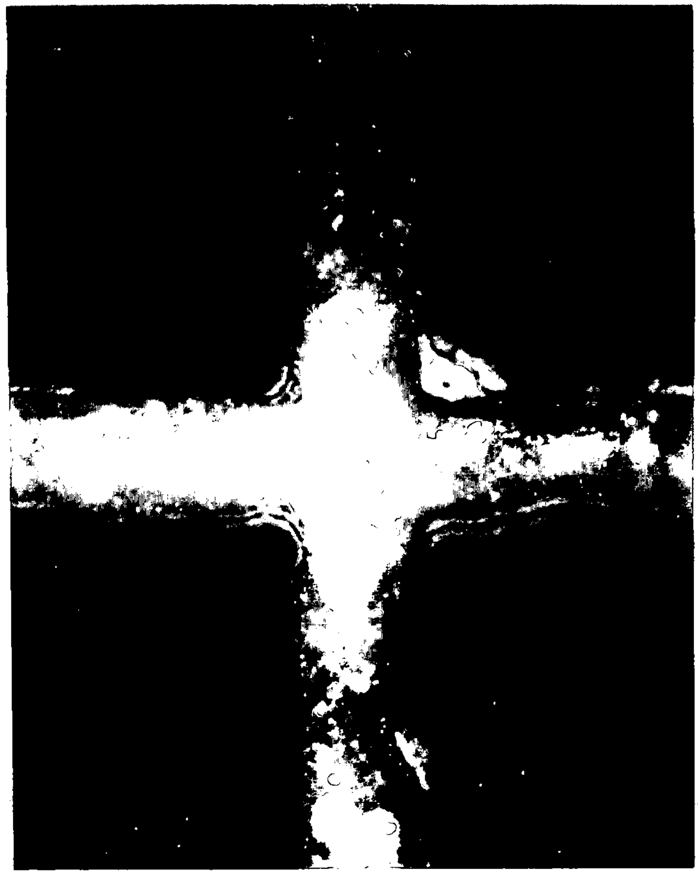
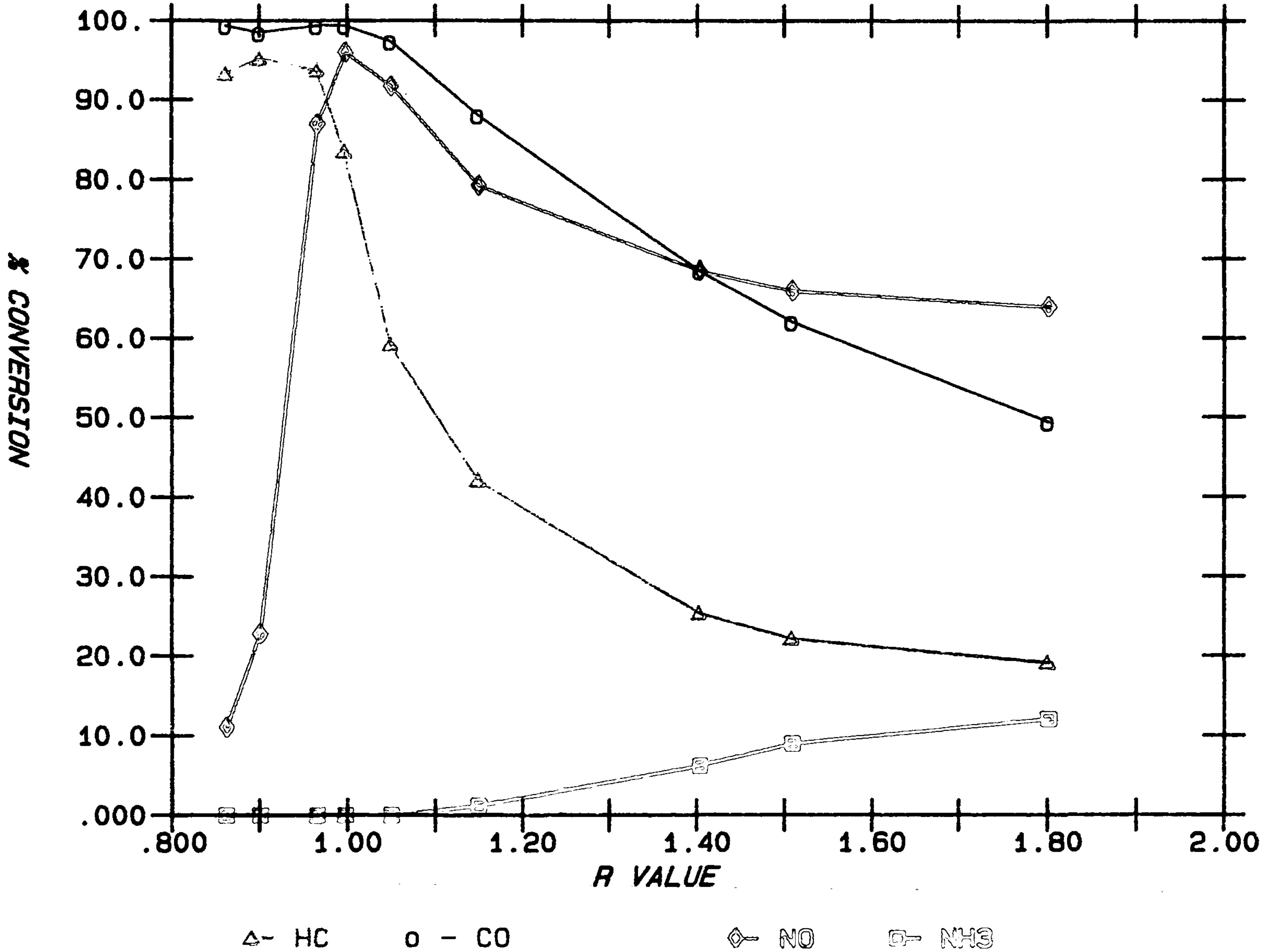


80X

xE 0

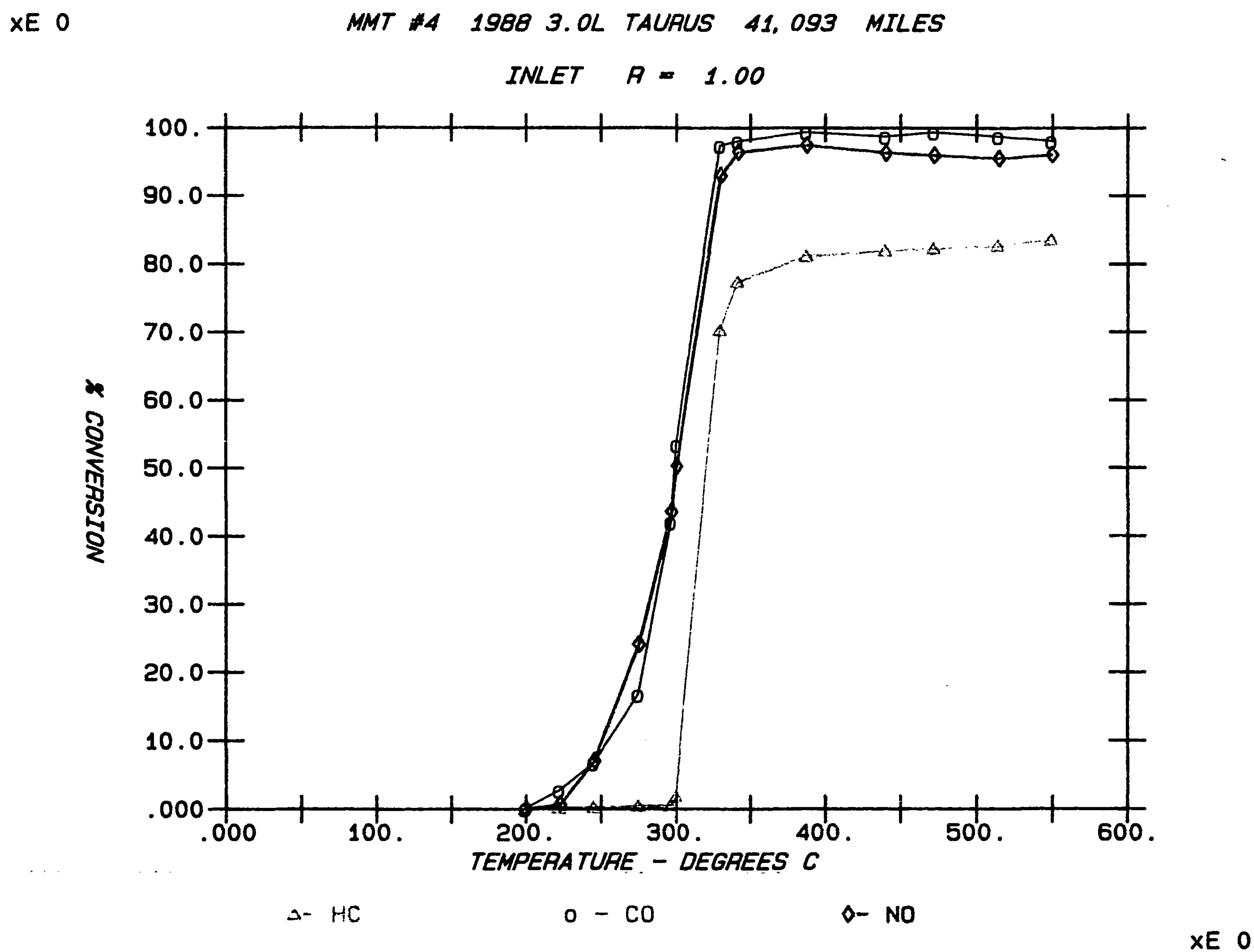
MMT #4 1988 3.0L TAURUS 41,093 MILES

INLET / 550. DEG.C



xE 0

45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MMT #4 1988 3.0L TAURUS 41,093 MILES
INLET R = 1.00
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90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
Δ- HC
o - CO
◊- NO
xE 0

Appendix E

1988 3.0L Sable

21,500 Miles

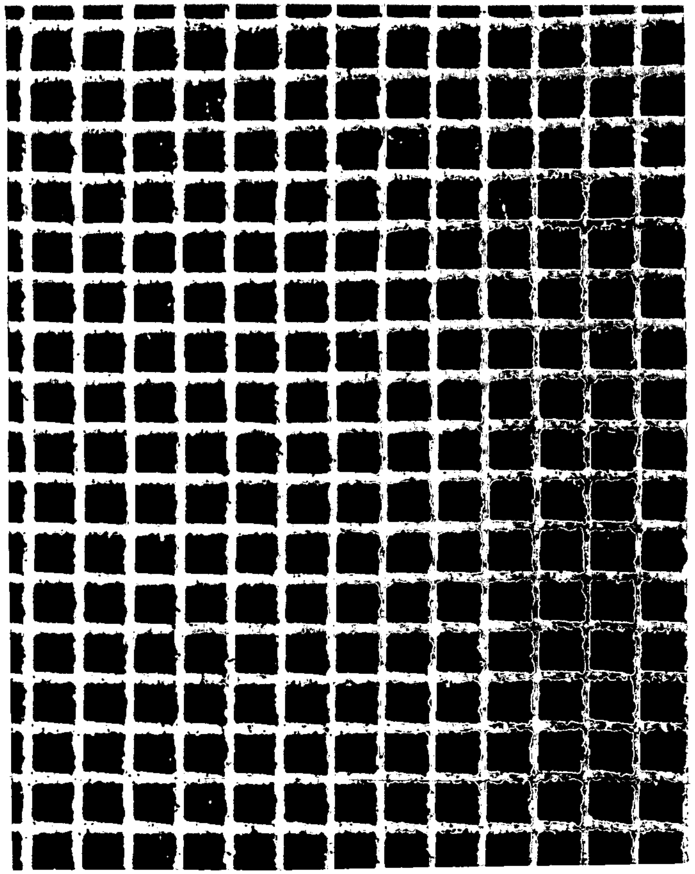
X-RAY FLUORESCENCE ANALYSIS OF MMT CATALYSTS

VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) CATALYTIC COMPONENTS PT	RH	PD	NI	CE	BA	LA	FE	g/ft^3	Pt/Pd/Rh
1988 3.0L Sable		**21,500 Miles**									
MMT-BK5I	15.9	.1838	.0397	.0000	.7859	6.3163	.7197	.2434	.4262	32.6	4.6/0/1.0
MMT-BK5M	13.6	.1896	.0412	.0000	.8266	6.4745	.7607	.2458	.4168	33.7	4.6/0/1.0
MMT-BK5O	13.5	.2012	.0448	.0000	.8219	6.2063	.8177	.2339	.4204	35.9	4.5/0/1.0
									Average:	34.1	4.6/0/1.0

VEHICLE CATALYST	CONTAMINATES PB	S	P	ZN	MN	CA	CL	CU
MMT-BK5I	.0387	.0435	.0959	.0460	.9464	.0150	.0000	.0268
MMT-BK5M	.0166	.0347	.0503	.0082	.4242	.0092	.0066	.0232
MMT-BK5O	.0137	.0332	.0358	.0063	.2913	.0095	.0316	.0234

1988 3.0L Sable- 21,500 Miles

Inlet



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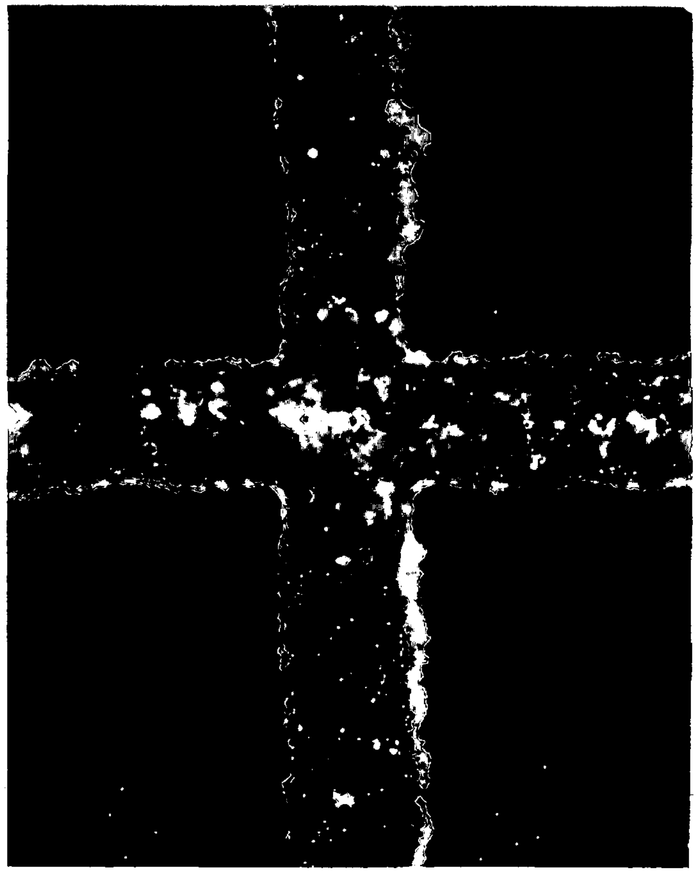

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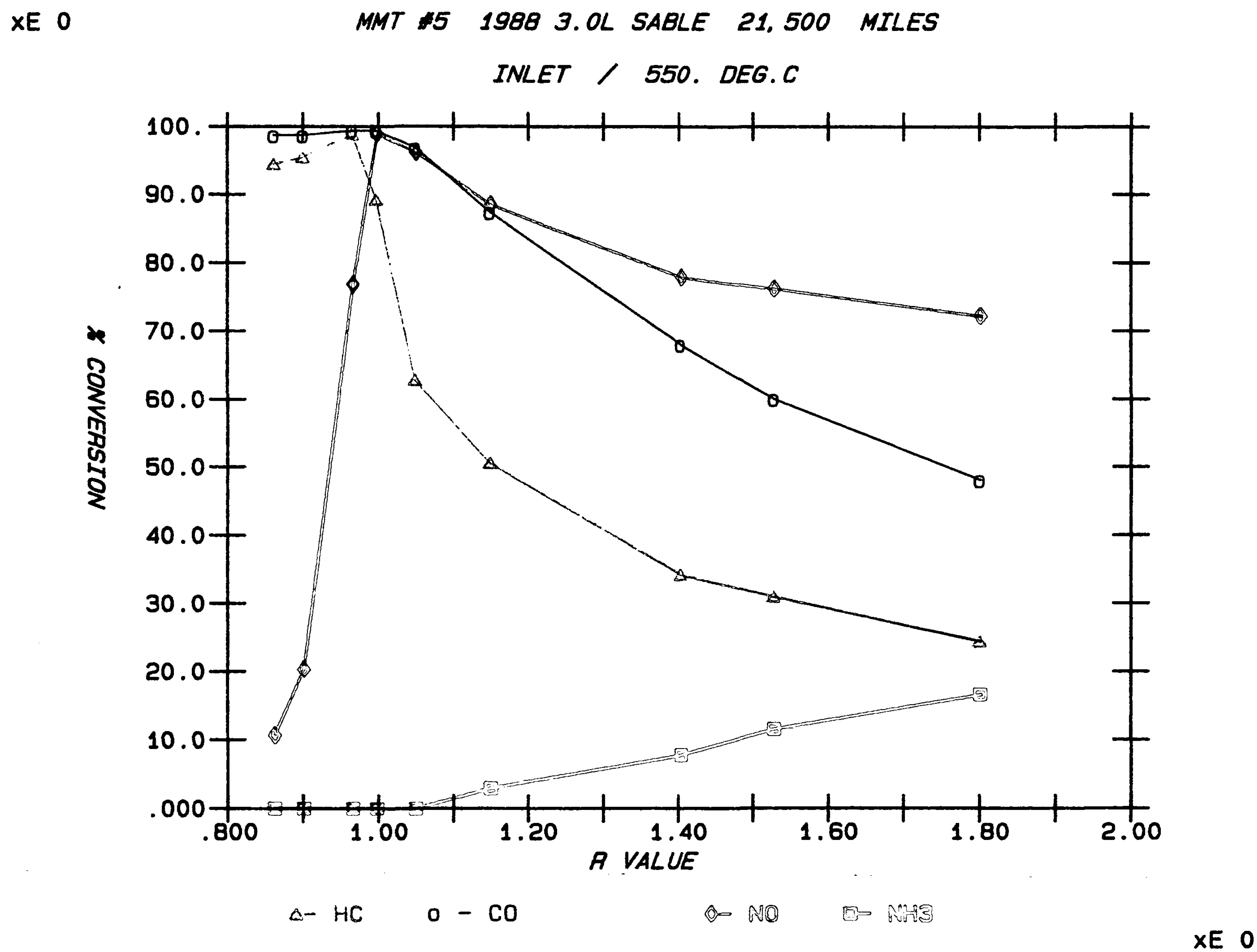

xE 0
MMT #5 1988 3.0L SABLE 21,500 MILES
INLET / 550. DEG.C
% CONVERSION
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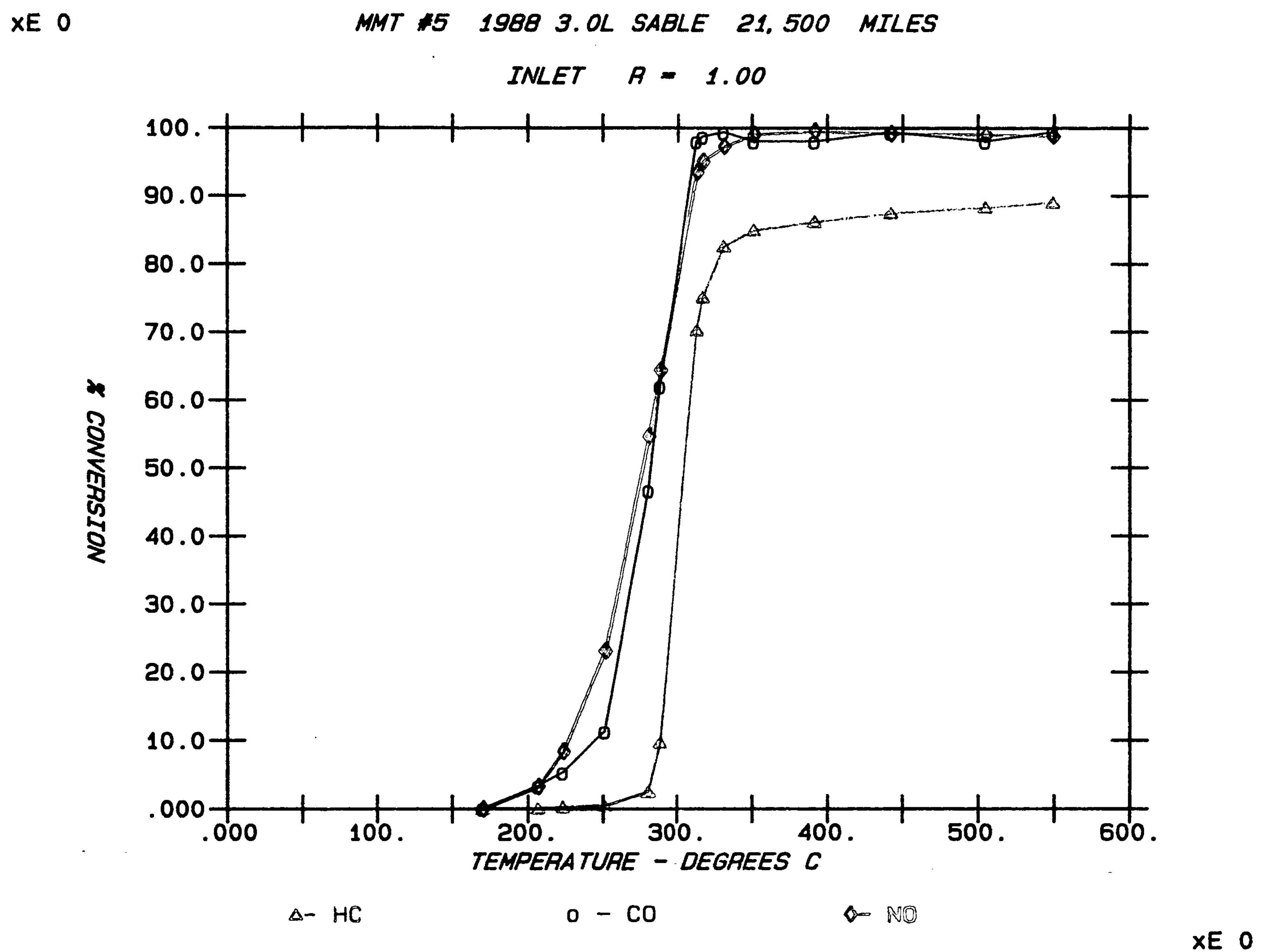
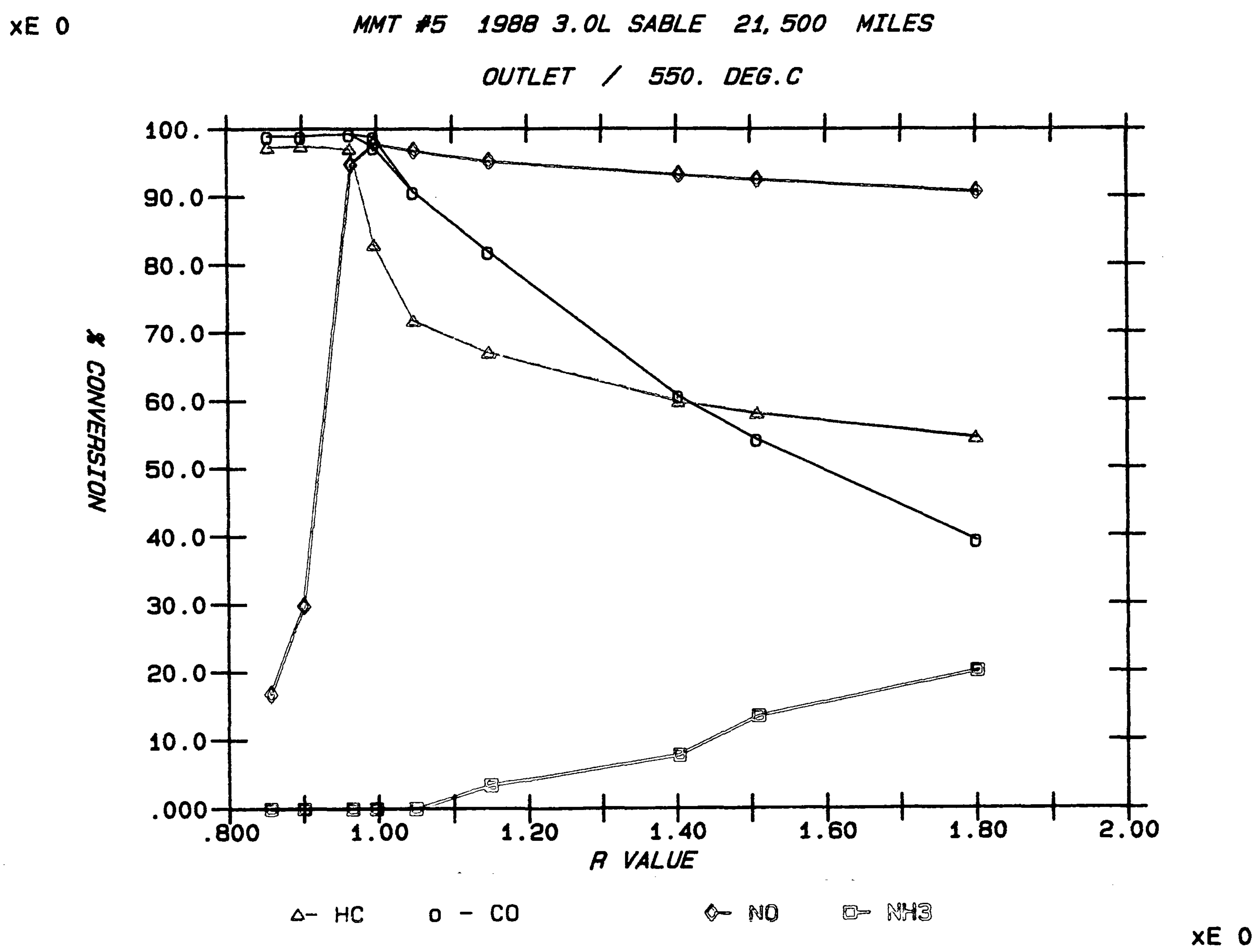
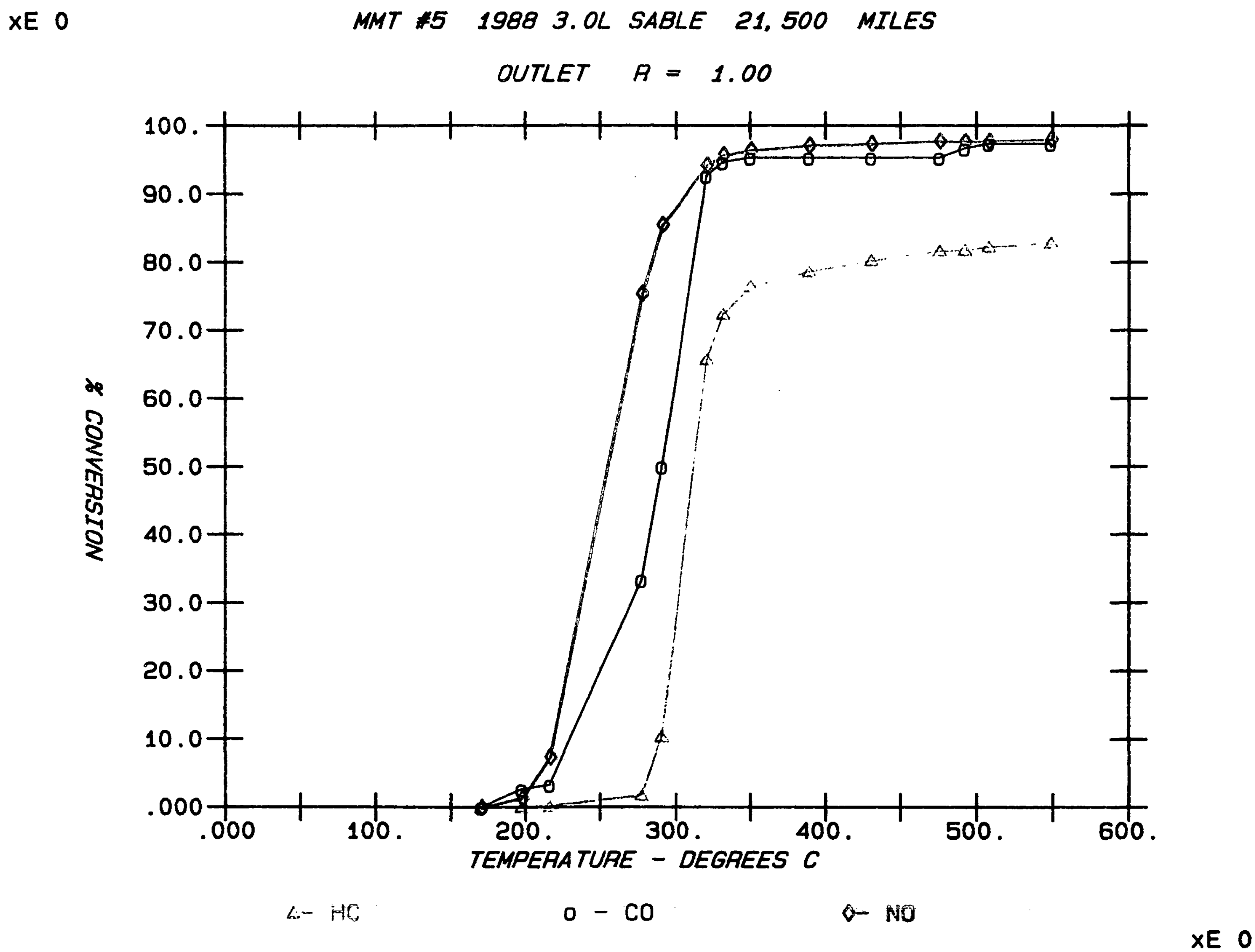
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
△- HC
o - CO
◇- NO
□- NH3
xE 0

50

5


xE 0
MMT #5 1988 3.0L SABLE 21,500 MILES
INLET R = 1.00
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
Δ- HC
o - CO
◇- NO
xE 0


xE 0
MMT #5 1988 3.0L SABLE 21,500 MILES
OUTLET / 550. DEG.C
% CONVERSION
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
HC
CO
NO
NH3
xE 0


xE 0
MMT #5 1988 3.0L SABLE 21,500 MILES
OUTLET R = 1.00
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
HC
o - CO
NO
xE 0

Appendix F

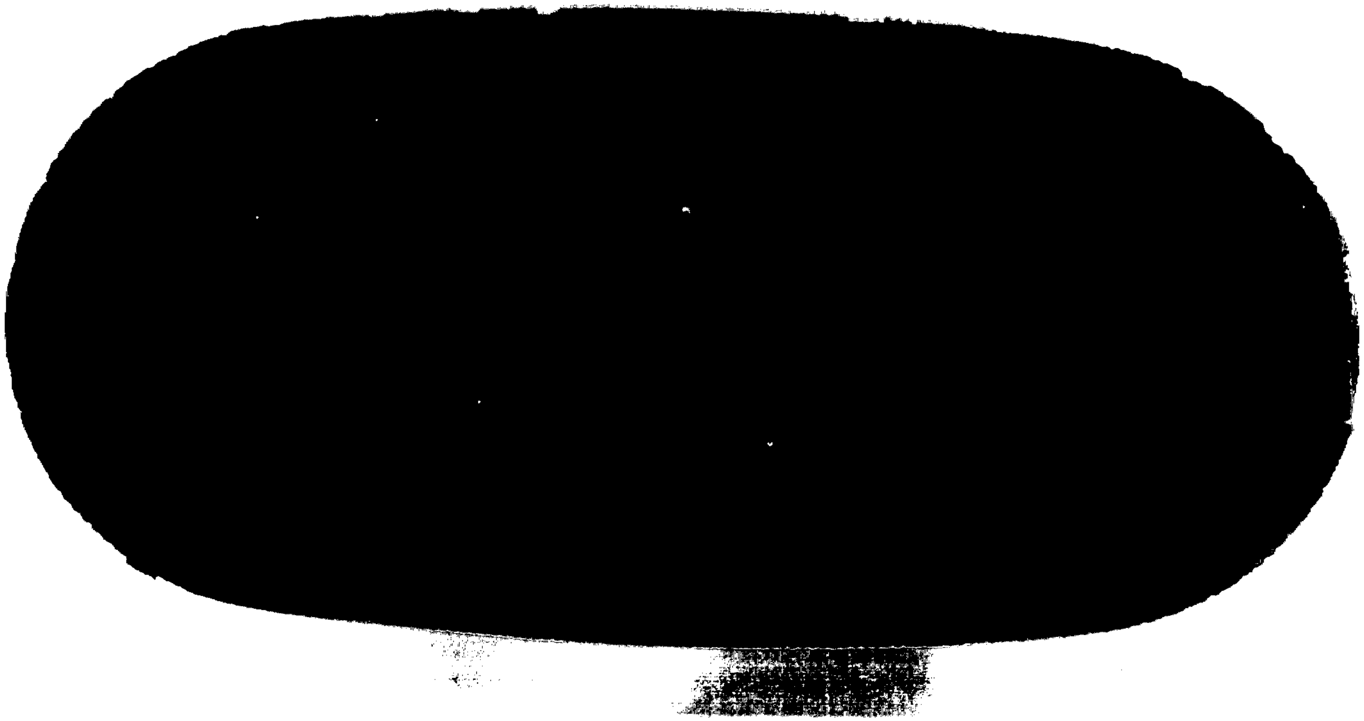
1987 3.0L Taurus

48,174 Miles

X-RAY FLUORESCENCE ANALYSIS OF MMT CATALYSTS

VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) CATALYTIC COMPONENTS PT	RH	PD	NI	CE	BA	LA	FE	g/ft^3	Pt/Pd/Rh
1987 3.0L Taurus		**48,174 Miles**									
MMT-BK6I	16.9	.1058	.0208	.0000	.7835	6.5841	.7865	.2452	.4071	18.5	5.1/0/1.0
MMT-BK6M	17.9	.1068	.0219	.0000	.8256	6.8790	.8273	.2593	.3606	18.8	4.9/0/1.0
MMT-BK6O	18.7	.1025	.0203	.0000	.8445	6.9089	.7971	.2602	.3644	17.9	5.0/0/1.0
									Average:	18.4	5.0/0/1.0

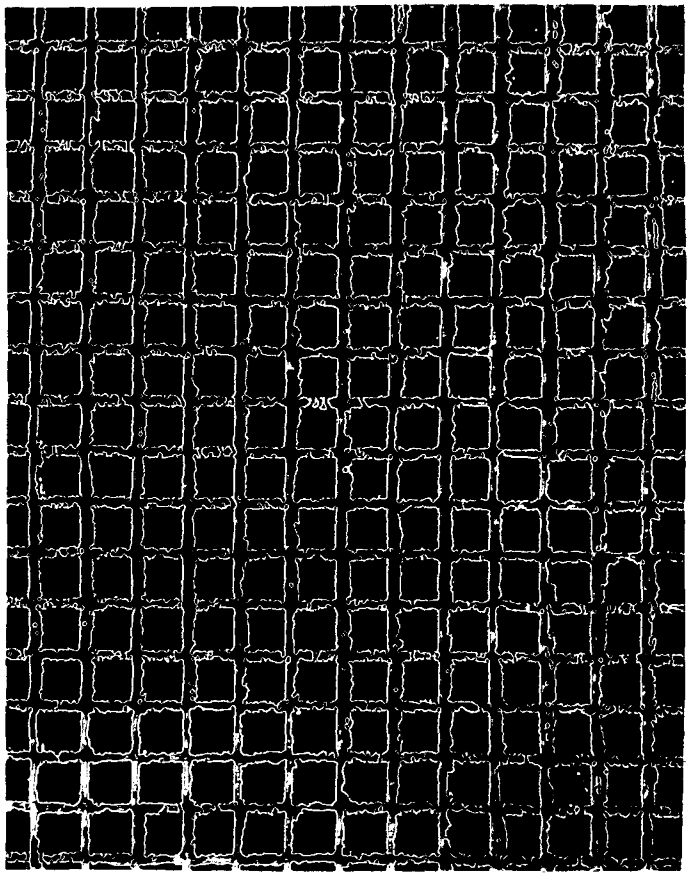
VEHICLE CATALYST	CONTAMINATES PB	S	P	ZN	MN	CA	CL	CU
MMT-BK6I	.1295	.0709	.1247	.0910	1.7447	.0859	.0000	.0241
MMT-BK6M	.0378	.0184	.0720	.0253	.9720	.0210	.0000	.0286
MMT-BK6O	.0242	.0067	.0555	.0163	.6614	.0179	.0000	.0213



1987 TAURUS
3.0L ENGINE
48,174 MILES

1987 3.0L Taurus- 48,174 Miles

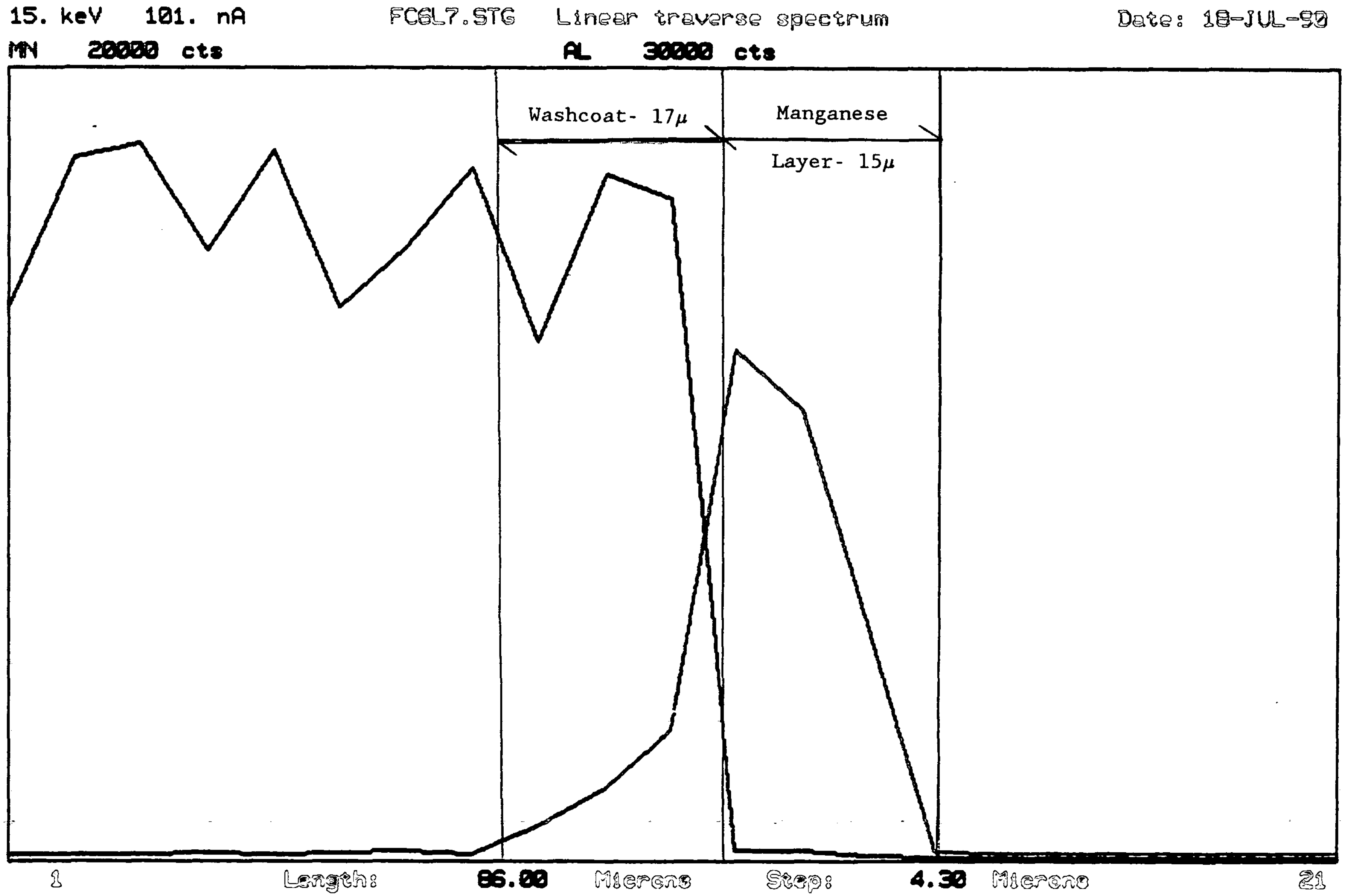
Inlet



5X

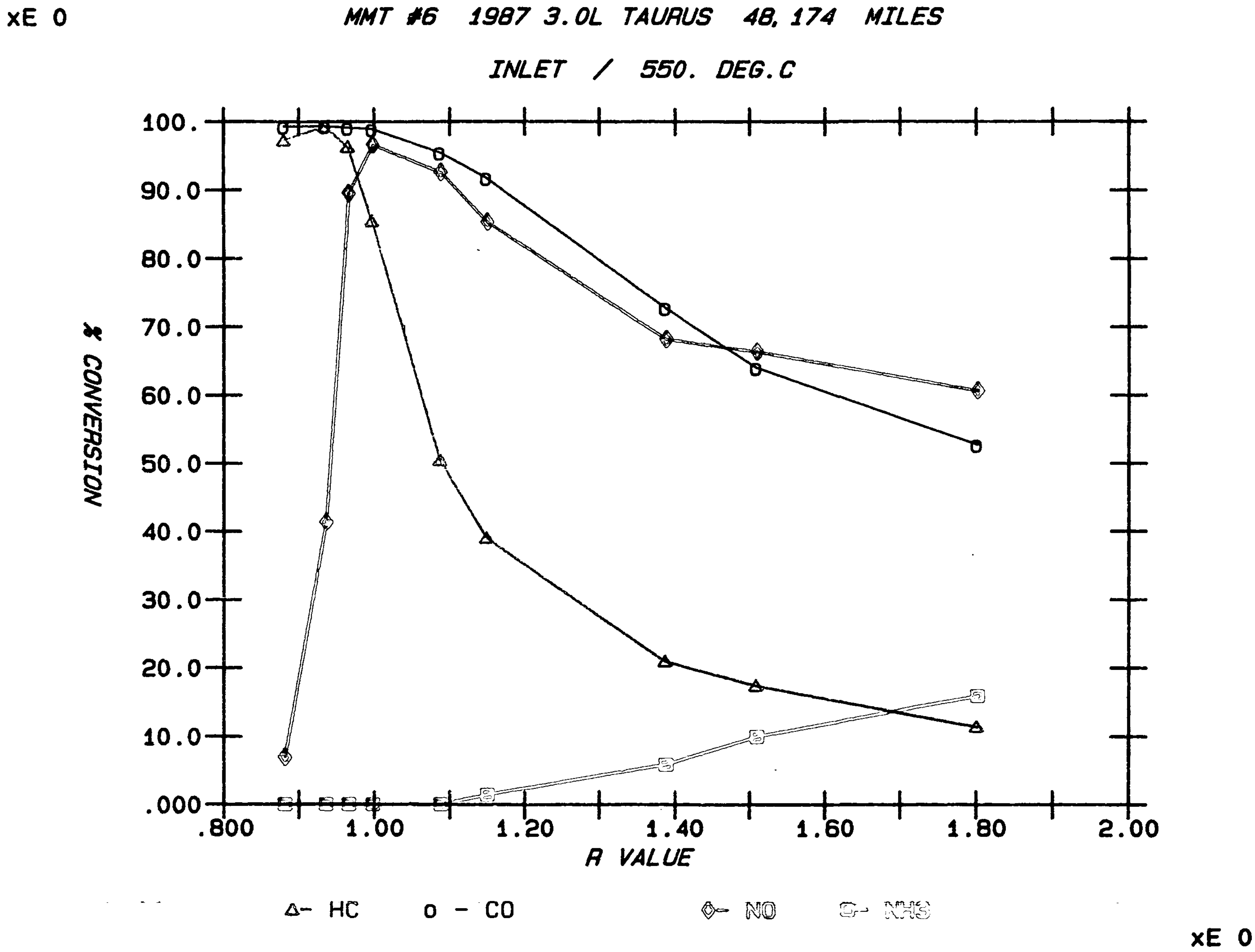
80X

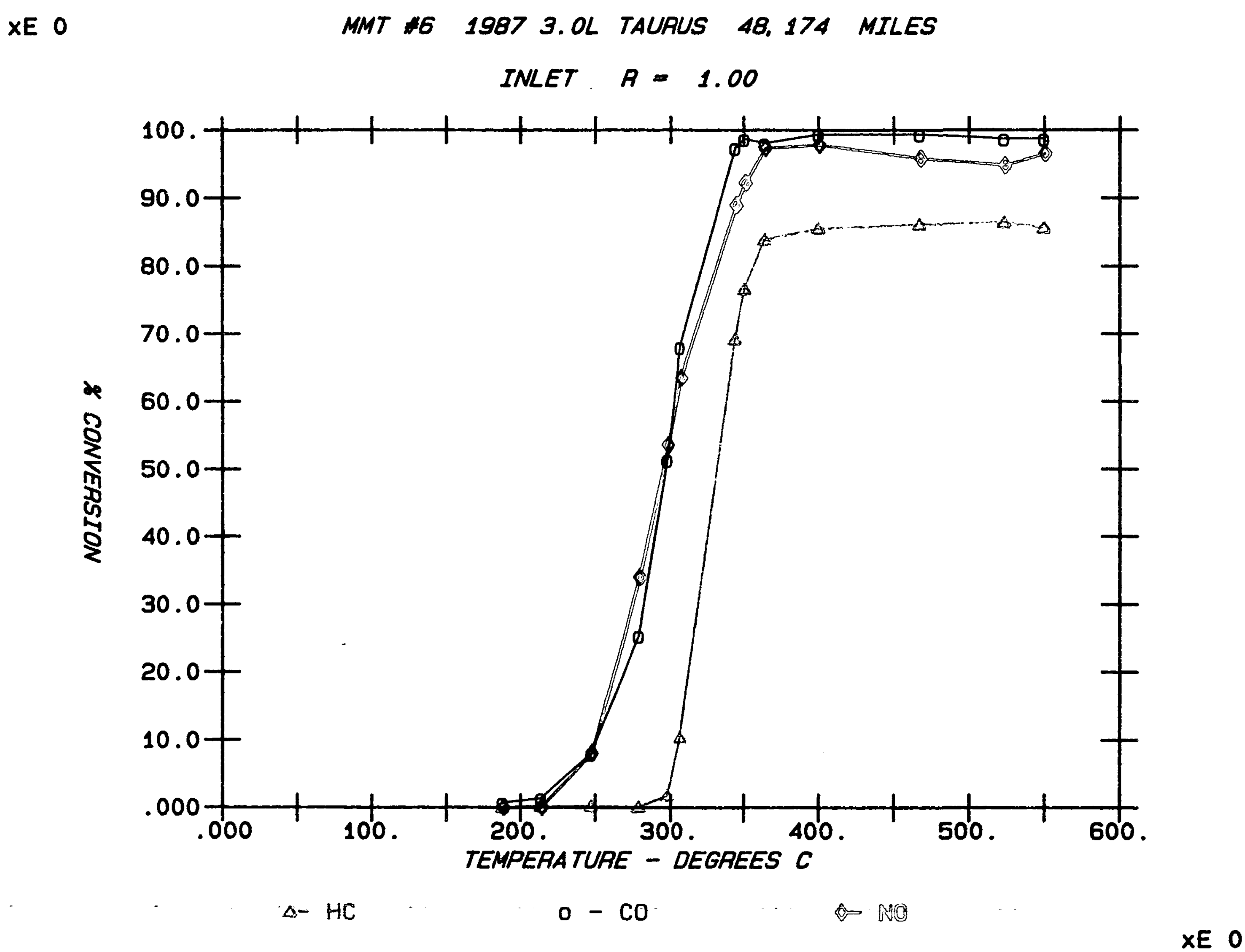
1987 3.0L Taurus- 48,174 Miles



MMT #6 1987 3.0L TAURUS 48,174 MILES

INLET / 550. DEG.C





xE 0
MMT #6 1987 3.0L TAURUS 48,174 MILES
INLET R = 1.00
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
Δ- HC
o - CO
◇- NO
xE 0

6

Appendix G

1988 3.8L Sable
62,224 Miles

X-RAY FLUORESCENCE ANALYSIS OF MMT CATALYSTS

VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) CATALYTIC COMPONENTS PT	RH	PD	NI	CE	BA	LA	FE	g/ft^3	Pt/Pd/Rh
1988 3.8L Sable		**62,224**									
MMT-BK7BI	17.5	.1297	.0256	.0000	.8338	6.5751	.8236	.2611	.3293	22.7	5.1/0/1.0
MMT-BK7BM	10.1	.1109	.0245	.0000	.7357	6.1638	.7311	.2439	.3410	19.8	4.5/0/1.0
MMT-BK7BO	8.4	.1163	.0259	.0000	.7354	6.3502	.8279	.2571	.3498	20.8	4.5/0/1.0
									Average:	21.1	4.7/0/1.0

VEHICLE CATALYST	CONTAMINATES PB	S	P	ZN	MN	CA	CL	CU
MMT-BK7BI	.1564	.0000	.2588	.3012	3.2341	.0478	.0000	.0314
MMT-BK7BM	.0476	.0000	.1422	.0892	1.8793	.0207	.0000	.0219
MMT-BK7BO	.0306	.0000	.1461	.0908	1.8992	.0304	.0000	.0206

X-RAY FLUORESCENCE ANALYSIS OF MMT CATALYSTS

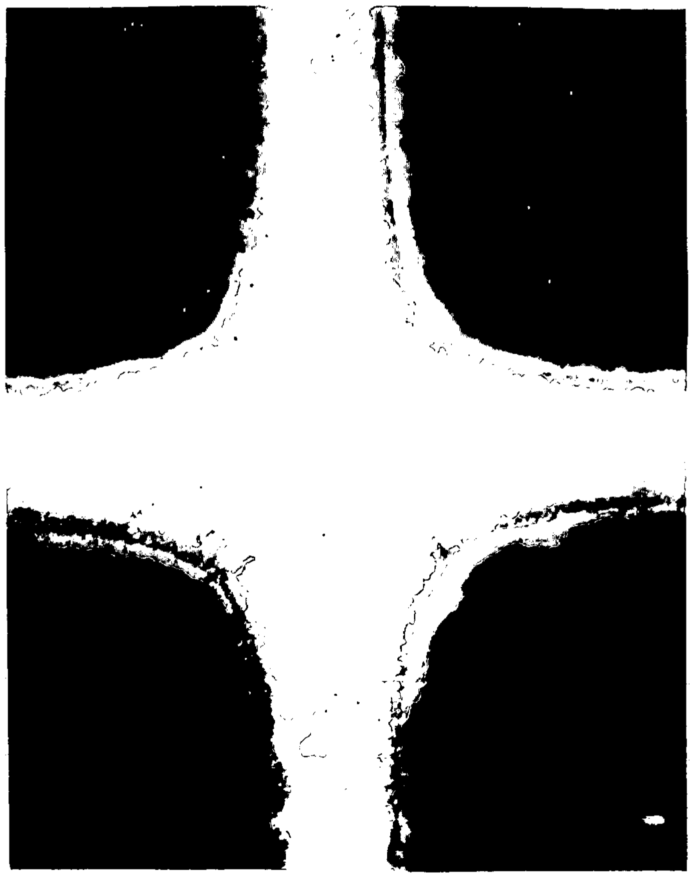
VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) CATALYTIC COMPONENTS PT	RH	PD	NI	CE	BA	LA	FE	g/ft^3	Pt/Pd/Rh
1988 3.8L Sable		**62,224 Miles**									
MMT-BK7AI	21.6	.1434	.0306	.0000	.6992	5.7912	.7650	.2309	.2985	25.4	4.7/0/1.0
MMT-BK7AM	19.7	.1317	.0281	.0000	.6584	5.6960	.7249	.2212	.2949	23.3	4.7/0/1.0
MMT-BK7AO	17.7	.1236	.0268	.0000	.6037	5.3997	.6719	.2085	.2970	21.9	4.6/0/1.0
									Average:	23.6	4.7/0/1.0

VEHICLE CATALYST	CONTAMINATES PB	S	P	ZN	MN	CA	CL	CU
MMT-BK7AI	.1785	.0000	.2079	.2091	2.0725	.0197	.0000	.0302
MMT-BK7AM	.0885	.0000	.1106	.0714	.9682	.0015	.0000	.0257
MMT-BK7AO	.0860	.0000	.0971	.0481	.9481	.0056	.0000	.0240

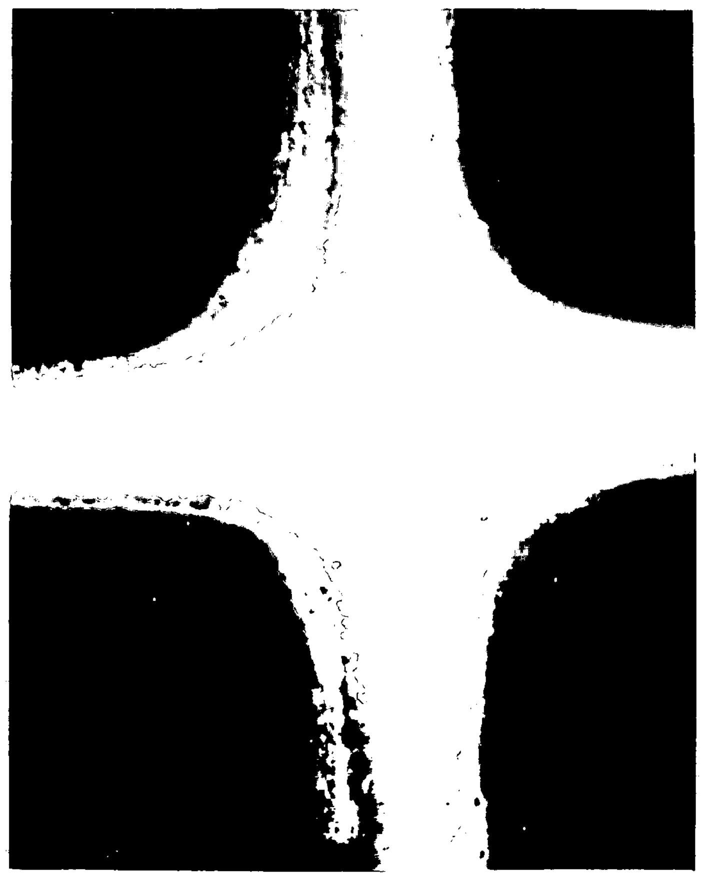
1988 SABLE
3.8L ENGINE
62,224 MILE

1988 3.8L Sable- 62,224 Miles

Inlet



7a 80X

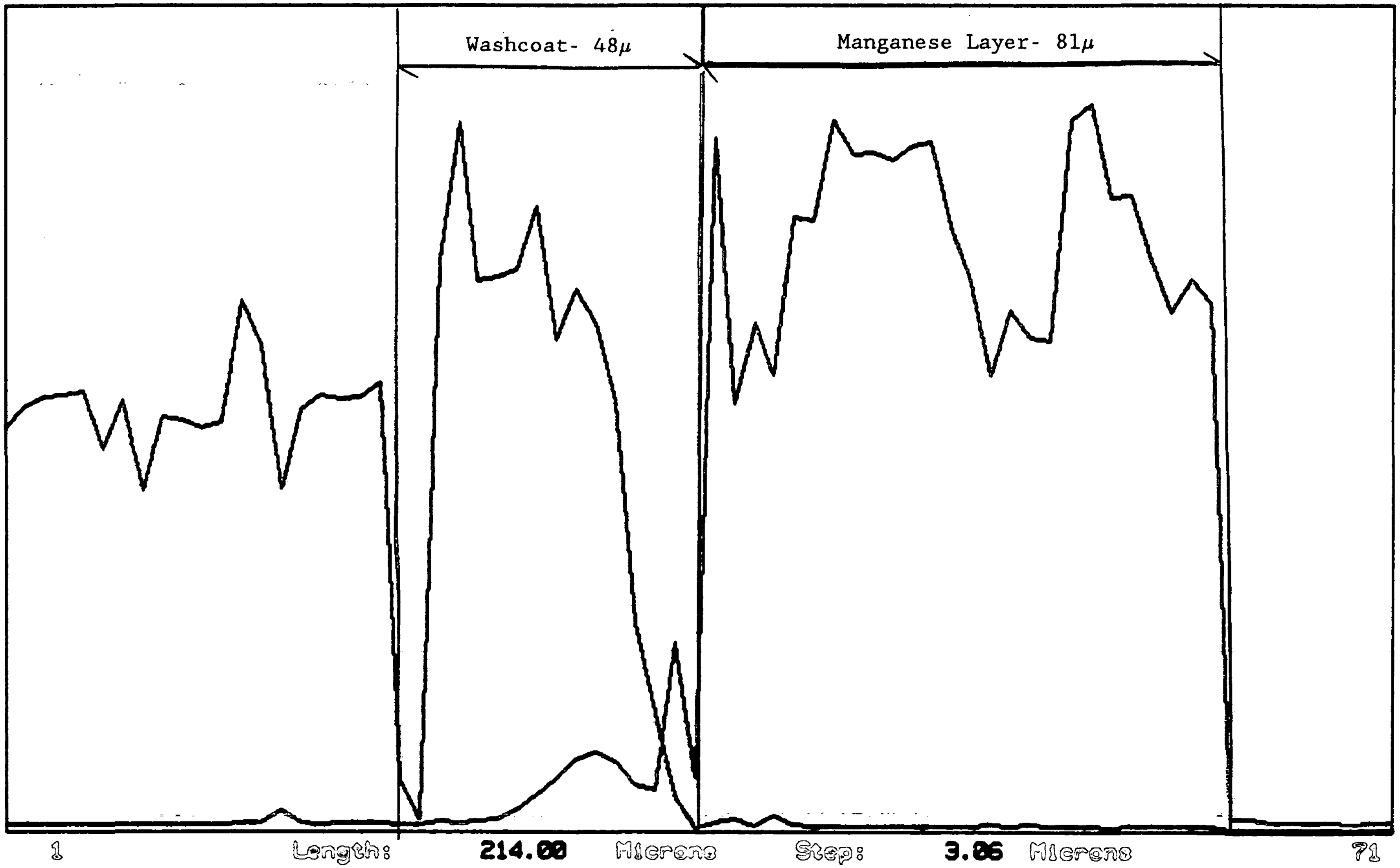


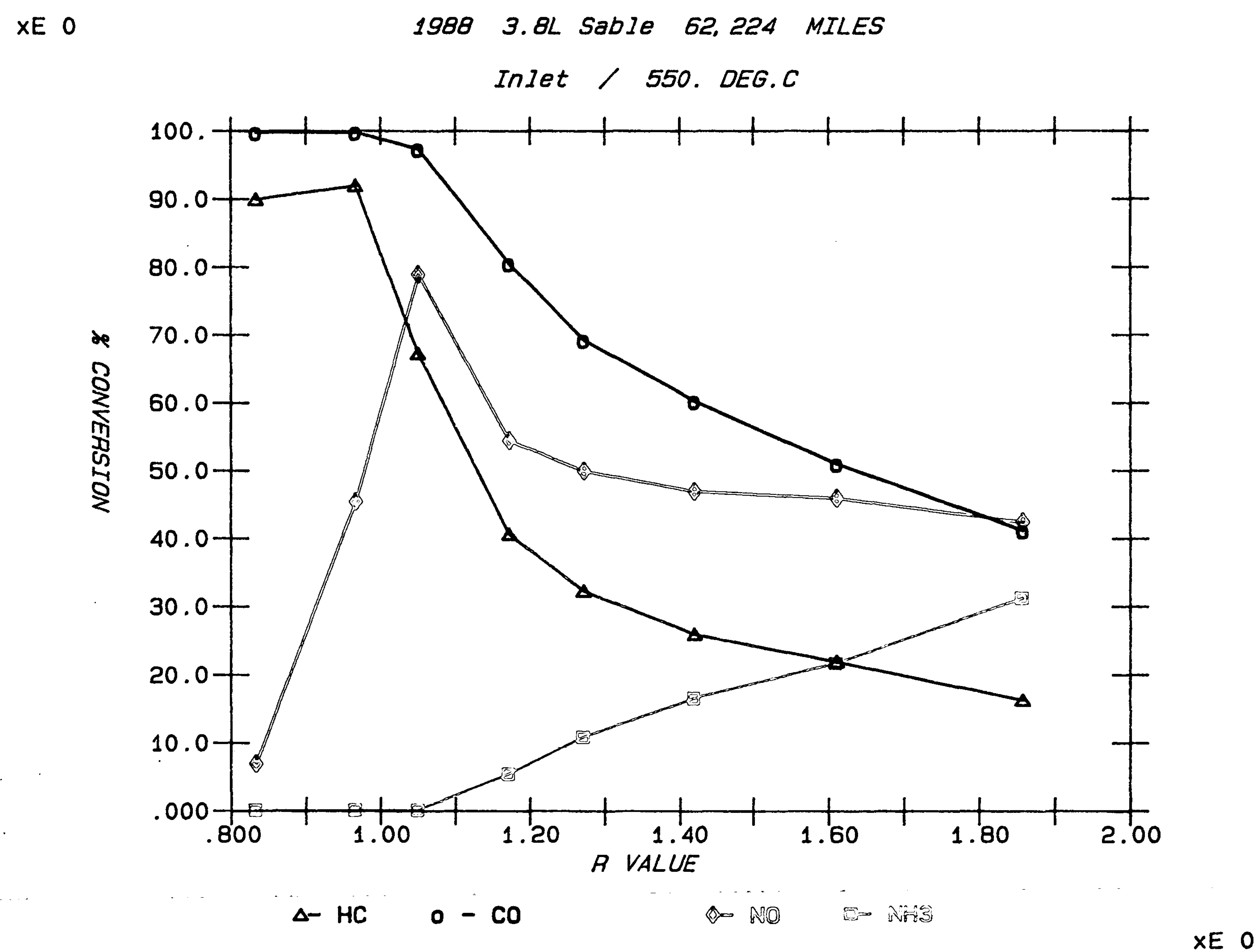
7b 80X

1988 3.8L Sable- 62,224 Miles

15. keV 100. nA FC78L6.STG Linear traverse spectrum Date: 18-JUL-90

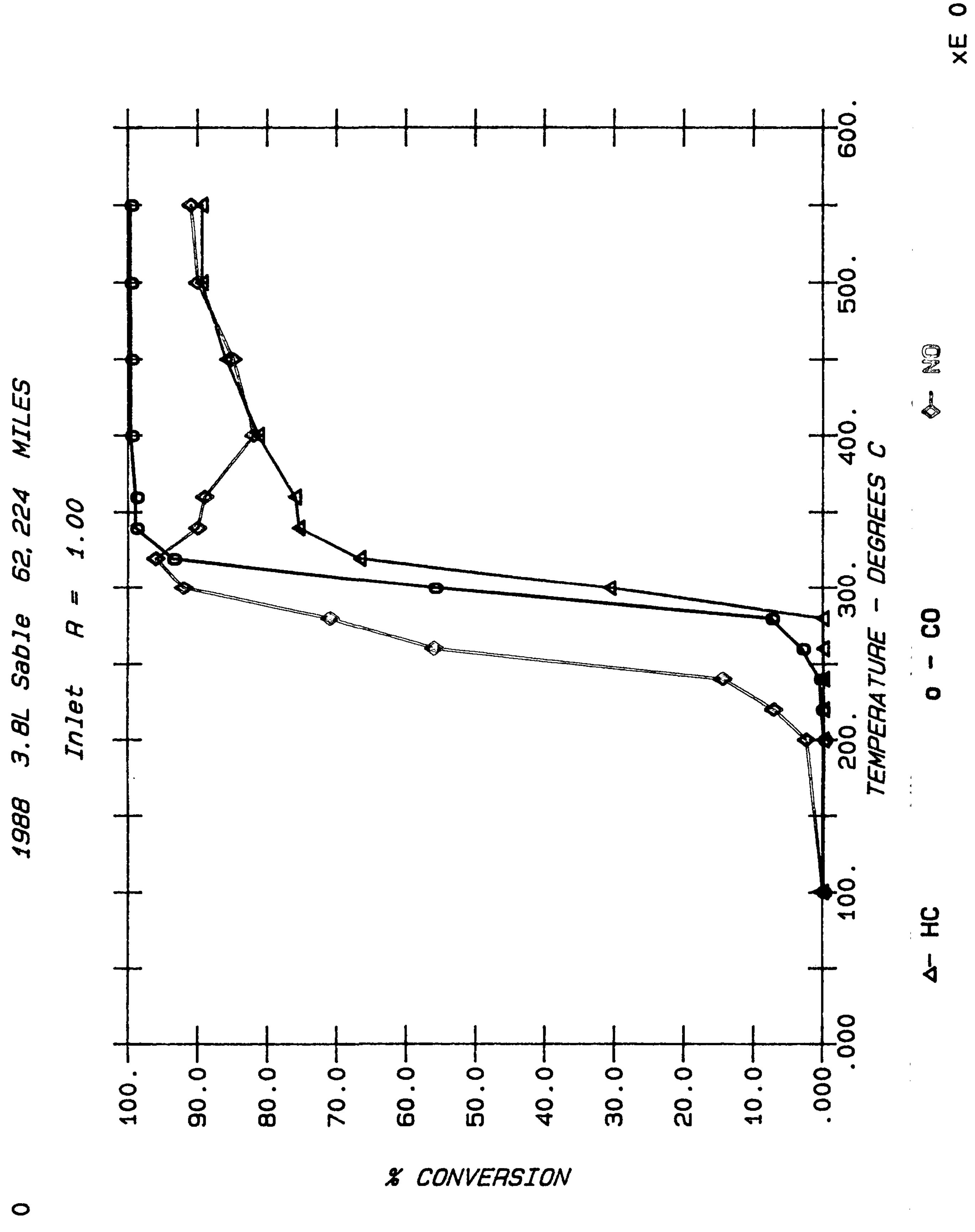
MN 20000 cts AL 50000 cts

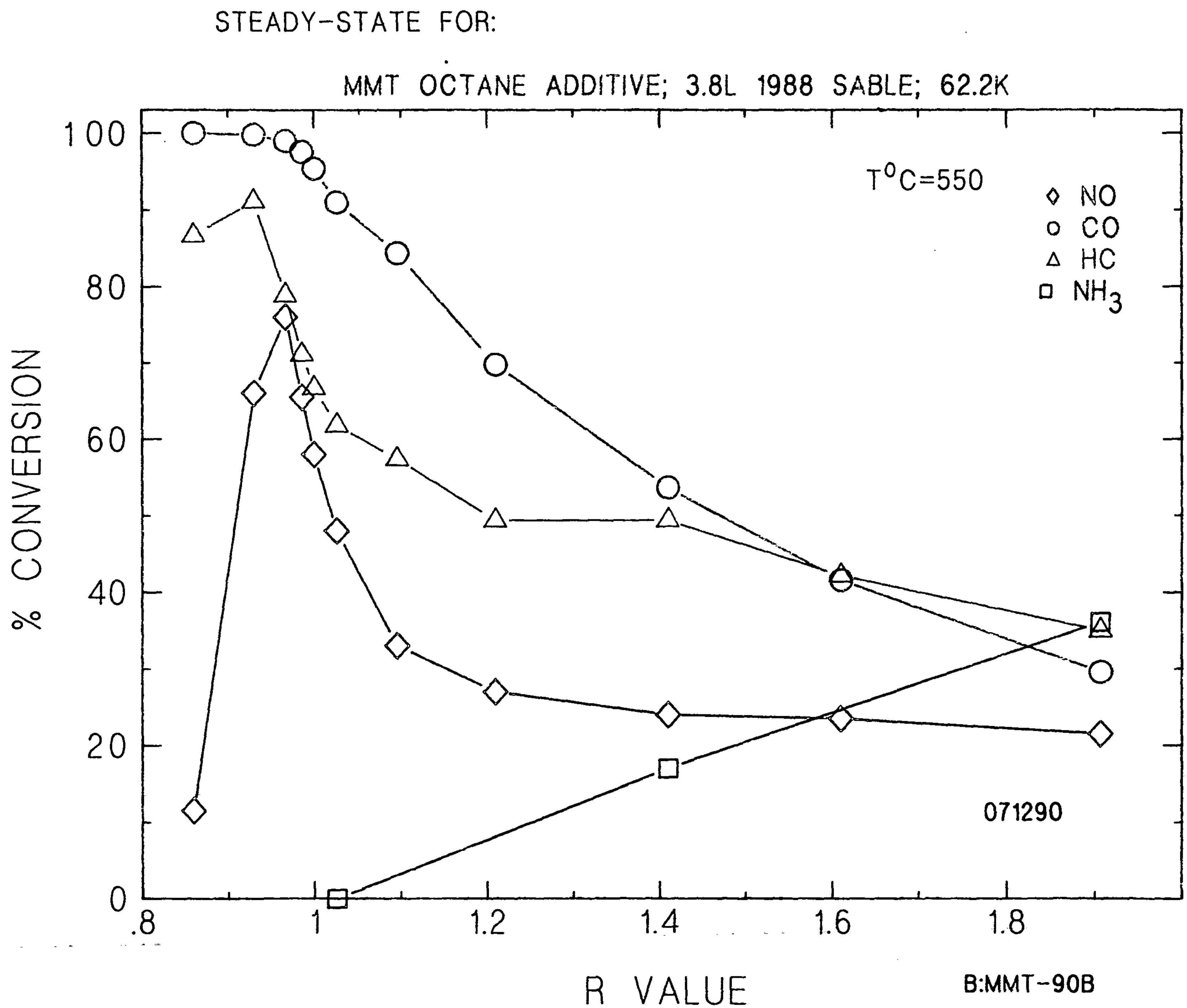



xE 0
1988 3.8L Sable 62,224 MILES
Inlet / 550. DEG.C
% CONVERSION
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
HC
CO
NO
NH3
xE 0

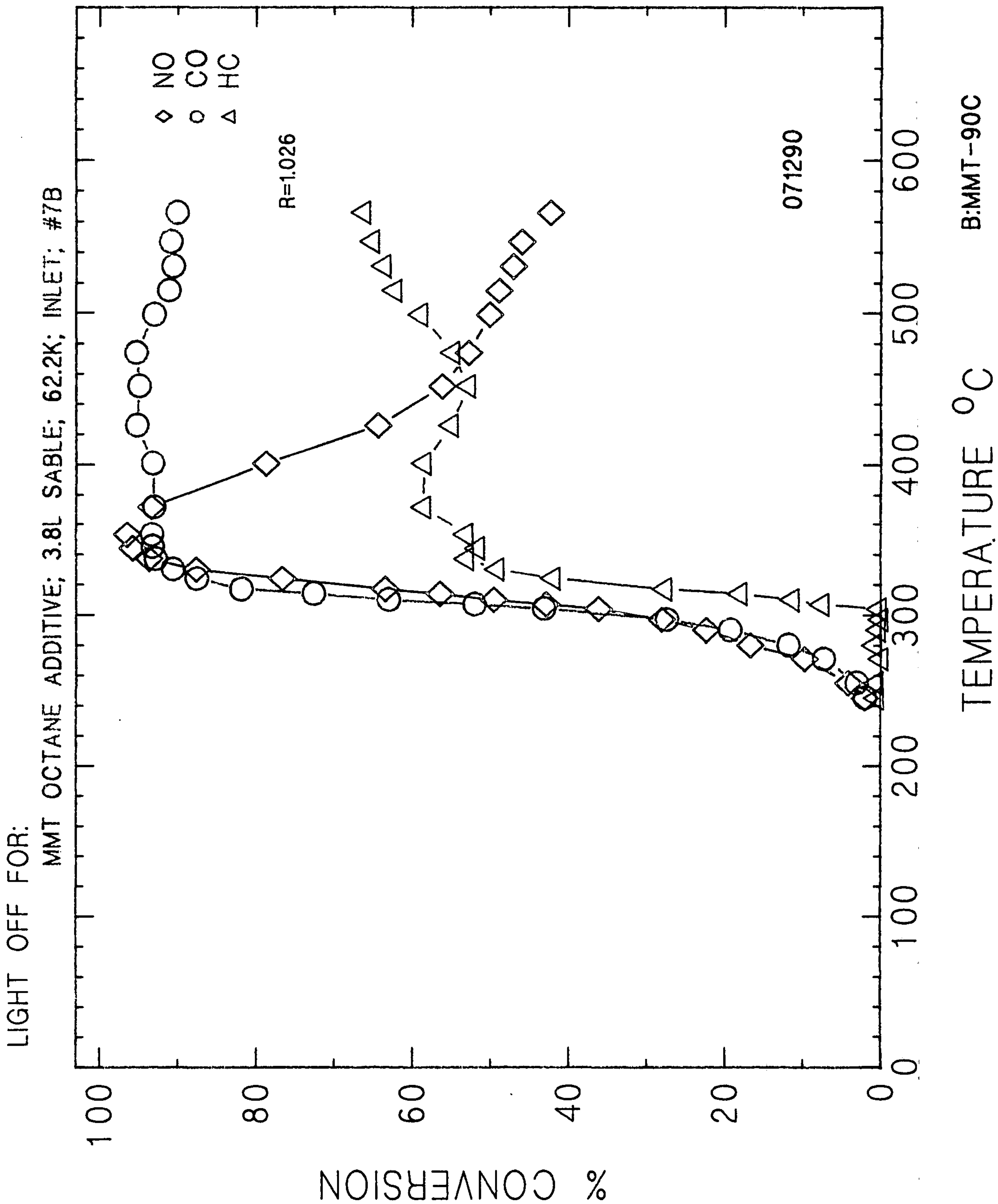
67

7


1988 3.8L Sable 62,224 MILES
Inlet R = 1.00
% CONVERSION
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
xE 0
xE 0
Δ- HC
o - CO
◇- NO

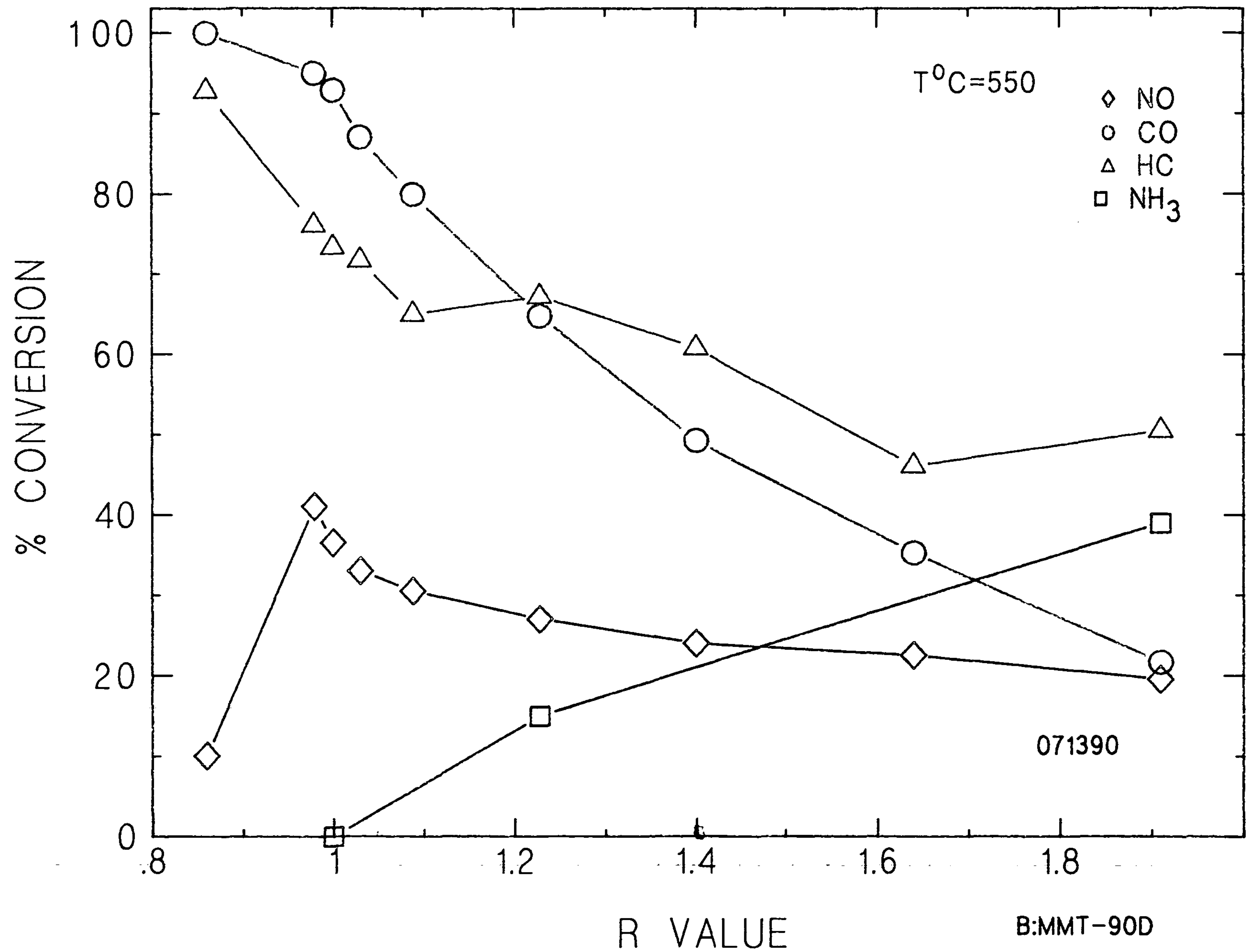


STEADY-STATE FOR:
MMT OCTANE ADDITIVE; 3.8L 1988 SABLE; 62.2K
T°C=550
NO
CO
HC
NH3
% CONVERSION
100
80
60
40
20
0
.8
1
1.2
1.4
1.6
1.8
R VALUE
071290
B:MMT-90B

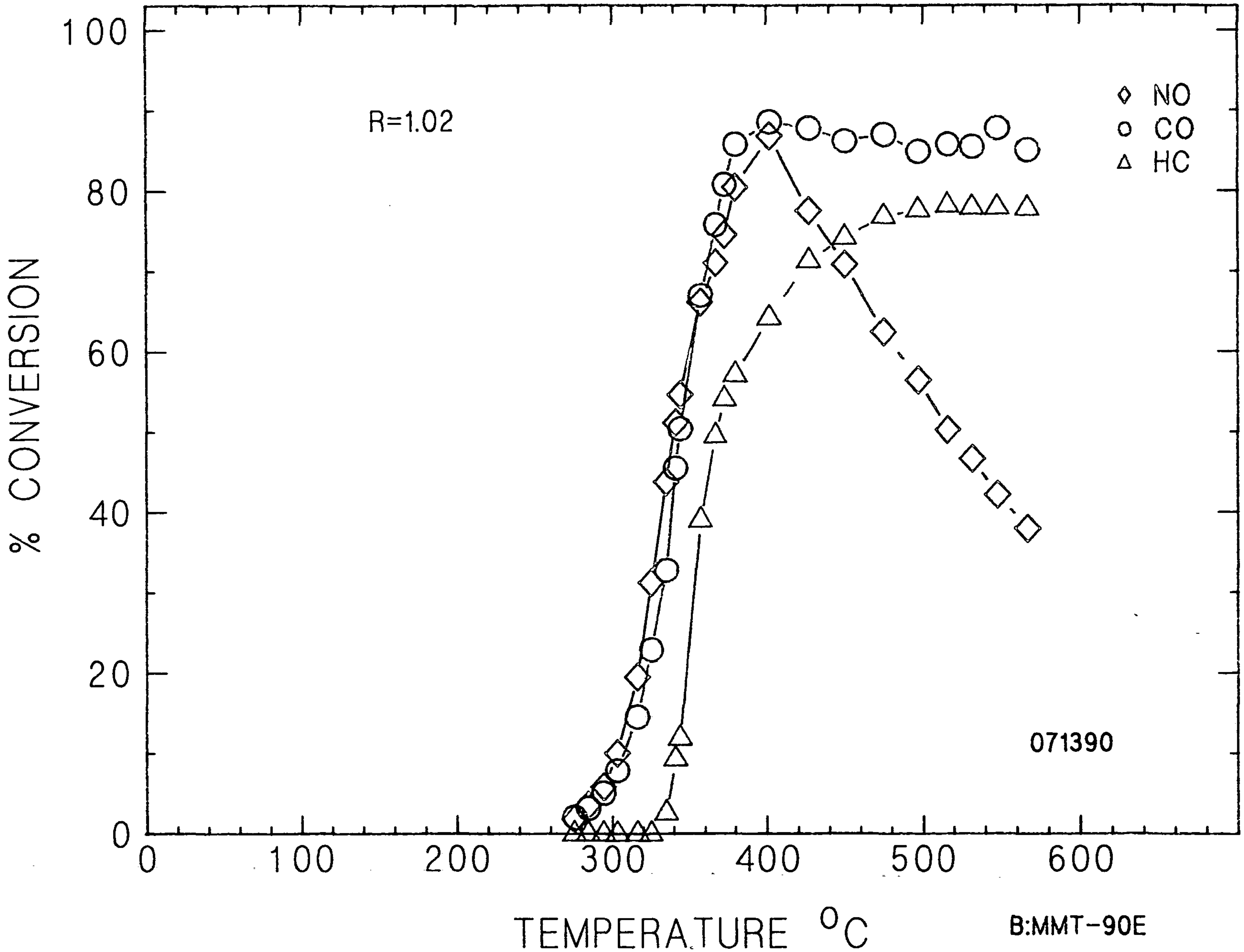

LIGHT OFF FOR:
MMT OCTANE ADDITIVE; 3.8L SABLE; 62.2K; INLET; #7B
◇ NO
○ CO
△ HC
R=1.026
071290
B:MMT-90C
TEMPERATURE °C
% CONVERSION
0
100
200
300
400
500
600
0
20
40
60
80
100

STEADY-STATE FOR:

MMT OCTANE ADDITIVE; 3.8L 1988 SABLE; 62.2K; OUTLET; #7B



LIGHT OFF FOR:
MMT OCTANE ADDITIVE; 3.8L 1988 SABLE; 62.2K; OUTLET; #7B



Appendix H

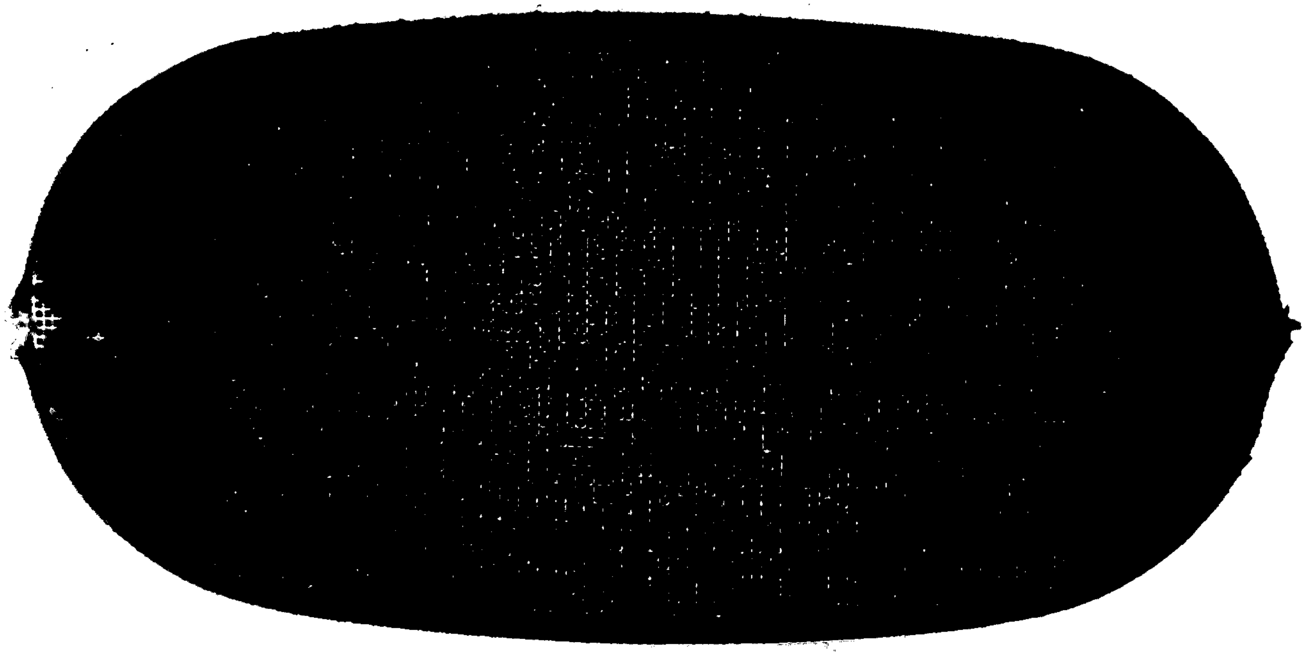
1987 3.0L Taurus

33,354 Miles

X-RAY FLUORESCENCE ANALYSIS OF MMT CATALYSTS

VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) CATALYTIC COMPONENTS PT	RH	PD	NI	CE	BA	LA	FE	g/ft^3	Pt/Pd/Rh
1987 3.0L Taurus		**33,354 Miles**									
MMT-BK8I	16.6	.0957	.0195	.0000	.6430	6.3581	.7382	.2752	.3026	16.8	4.9/0/1.0
MMT-BK8M	18.1	.0992	.0206	.0000	.6835	6.5212	.7867	.2775	.2614	17.5	4.8/0/1.0
MMT-BK8O	15.0	.1000	.0191	.0000	.6737	6.3627	.7749	.2711	.2661	17.4	5.2/0/1.0
									Average:	17.2	5.0/0/1.0

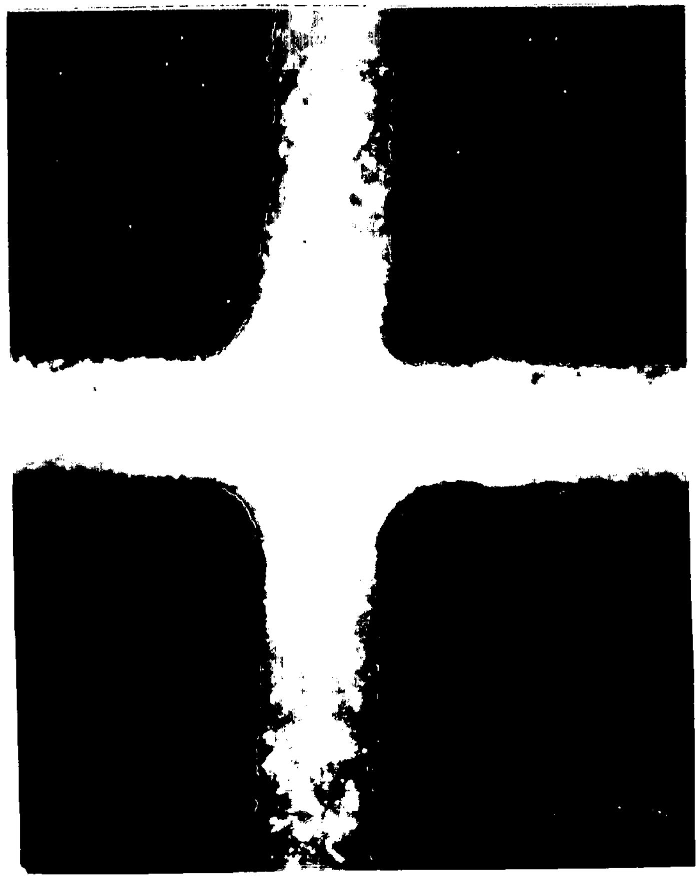
VEHICLE CATALYST	CONTAMINATES PB	S	P	ZN	MN	CA	CL	CU
MMT-BK8I	.2153	.0594	.1569	.1083	1.2705	.0532	.0000	.0310
MMT-BK8M	.0673	.0314	.0779	.0270	.5982	.0093	.0000	.0264
MMT-BK8O	.0453	.0463	.0648	.0184	.4806	.0084	.0000	.0248



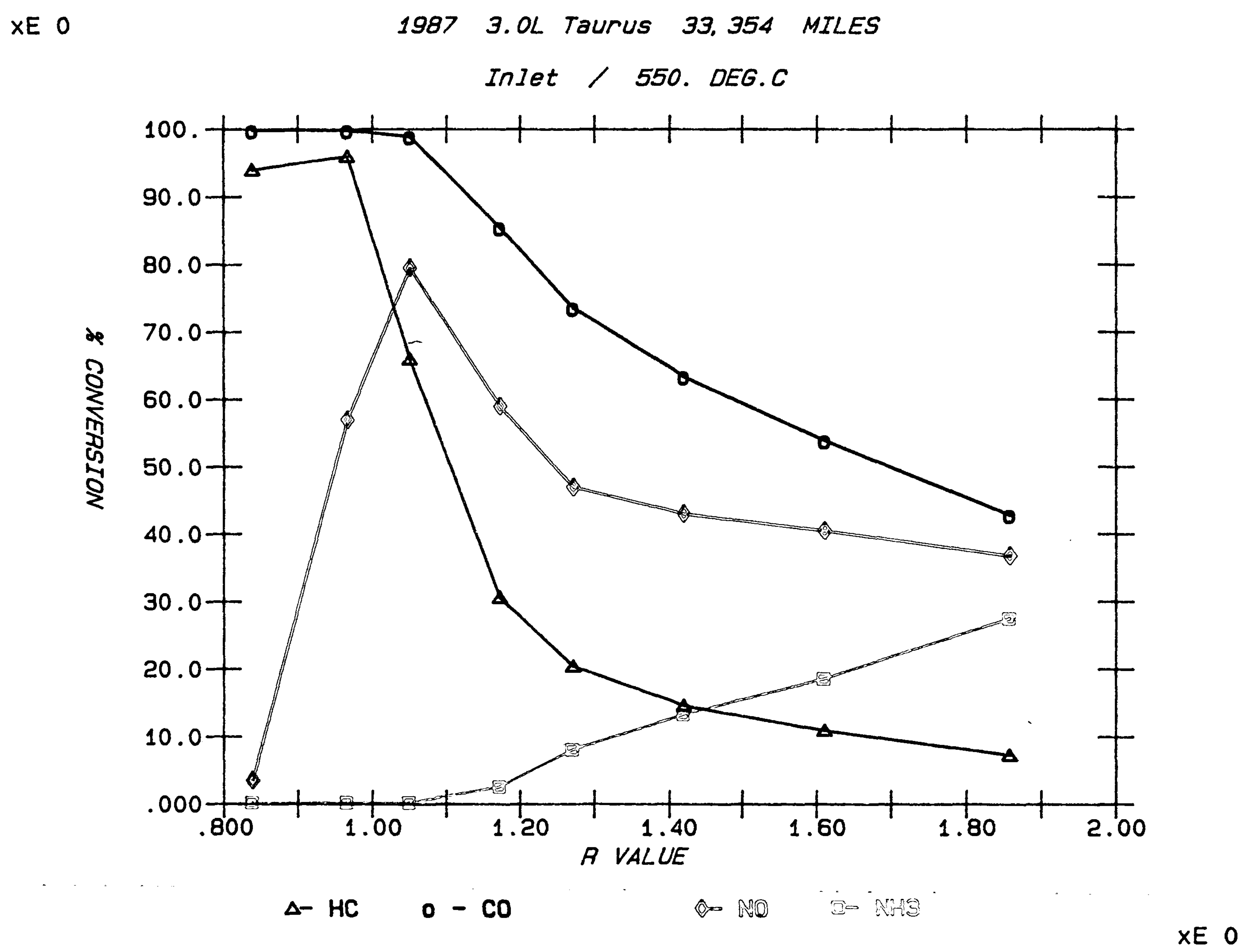
1987 TAURUS
3.0L ENGINE
33,354 MILE

1987 3.0L Taurus- 33,354 Miles

Inlet



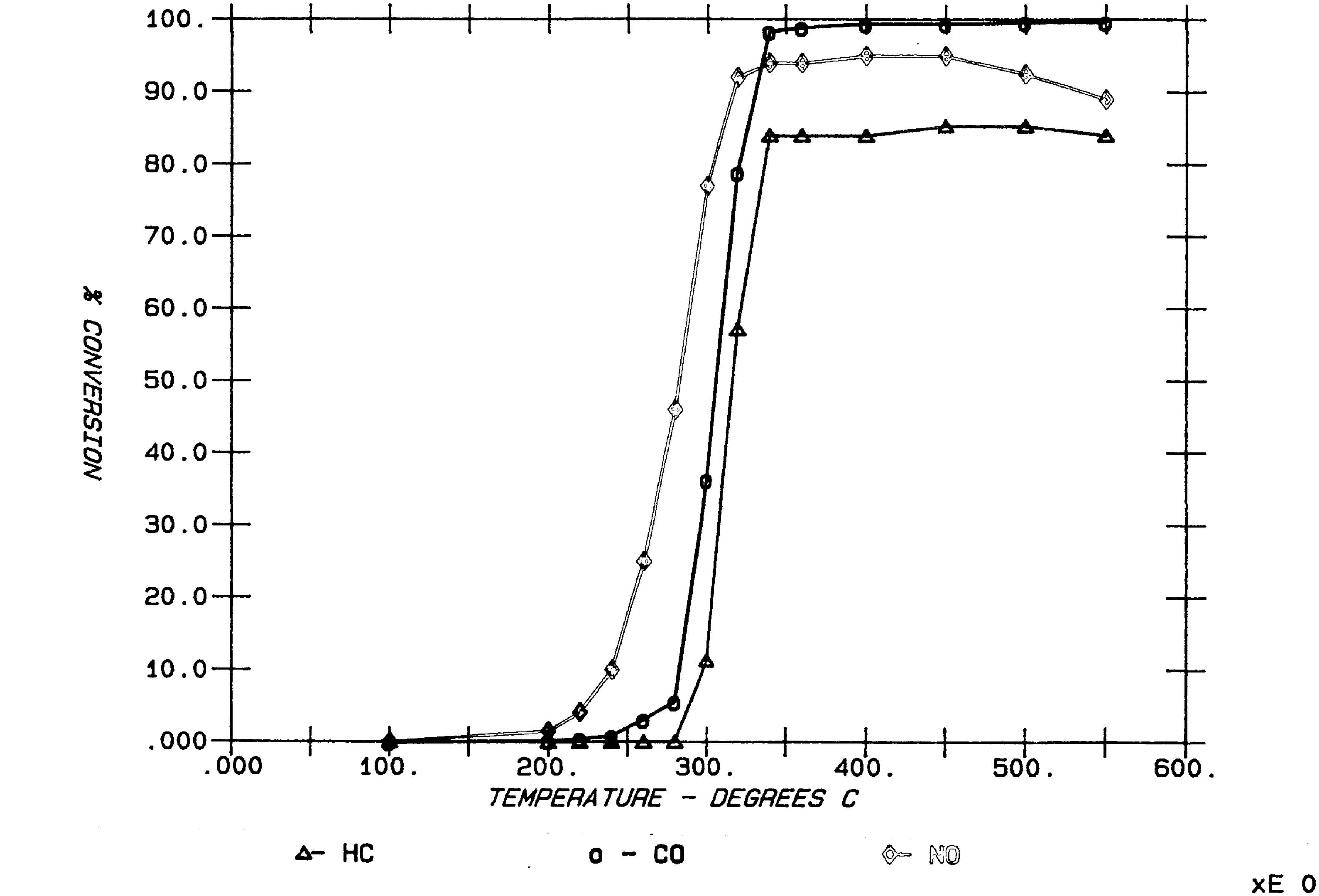
80X



xE 0
1987 3.0L Taurus 33,354 MILES
Inlet / 550. DEG.C
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
xE 0
HC
CO
NO
NH3

1987 3.0L Taurus 33,354 MILES

Inlet R = 1.00



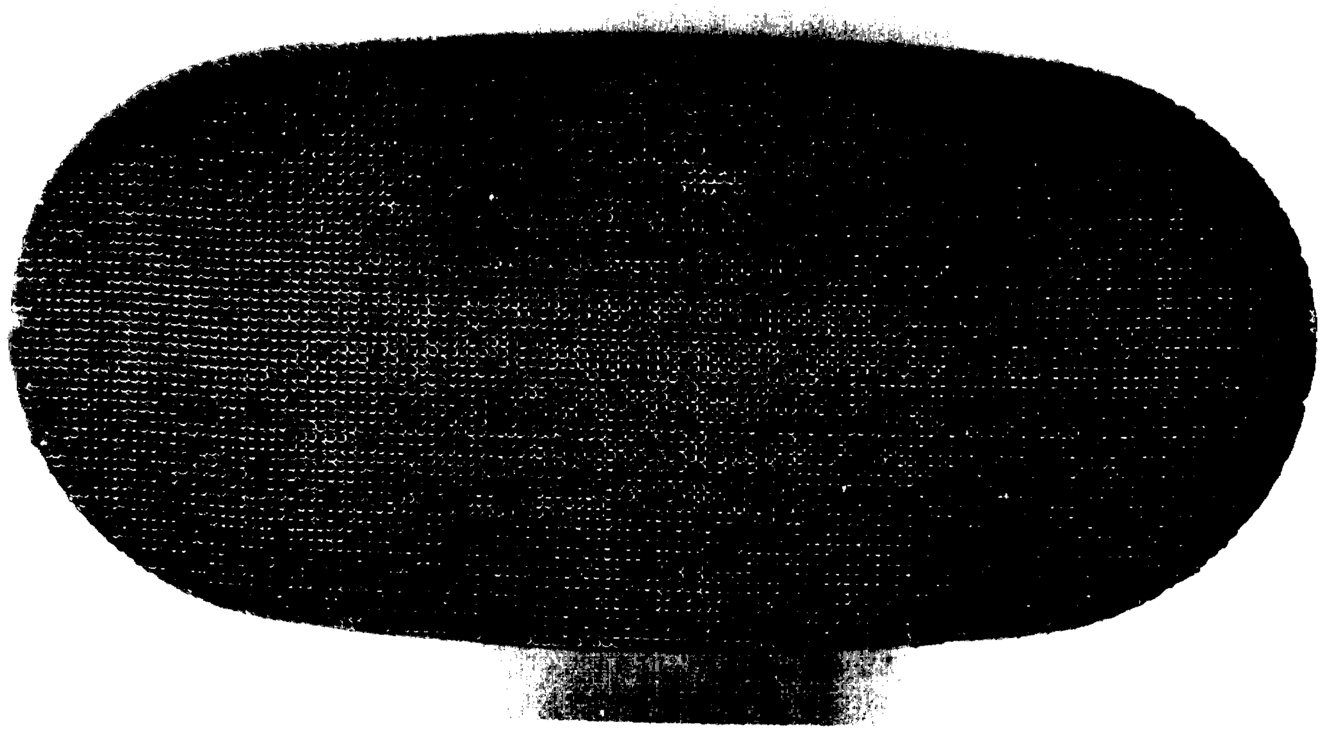
Appendix I

1988 3.0L Sable
27,416 Miles

X-RAY FLUORESCENCE ANALYSIS OF MMT CATALYSTS

VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) CATALYTIC COMPONENTS PT	RH	PD	NI	CE	BA	LA	FE	g/ft^3	Pt/Pd/Rh
1988 3.0L Sable		**27,416 Miles**									
MMT-BK9I	19.2	.2302	.0463	.0000	.8121	5.4610	.8382	.2047	.3127	40.4	5.0/0/1.0
MMT-BK9M	19.1	.1943	.0391	.0000	.7457	5.3560	.7030	.2018	.2926	34.4	5.0/0/1.0
MMT-BK9O	19.9	.1964	.0386	.0000	.7443	5.3895	.8043	.2022	.3113	34.3	5.1/0/1.0
									Average:	36.2	5.0/0/1.0

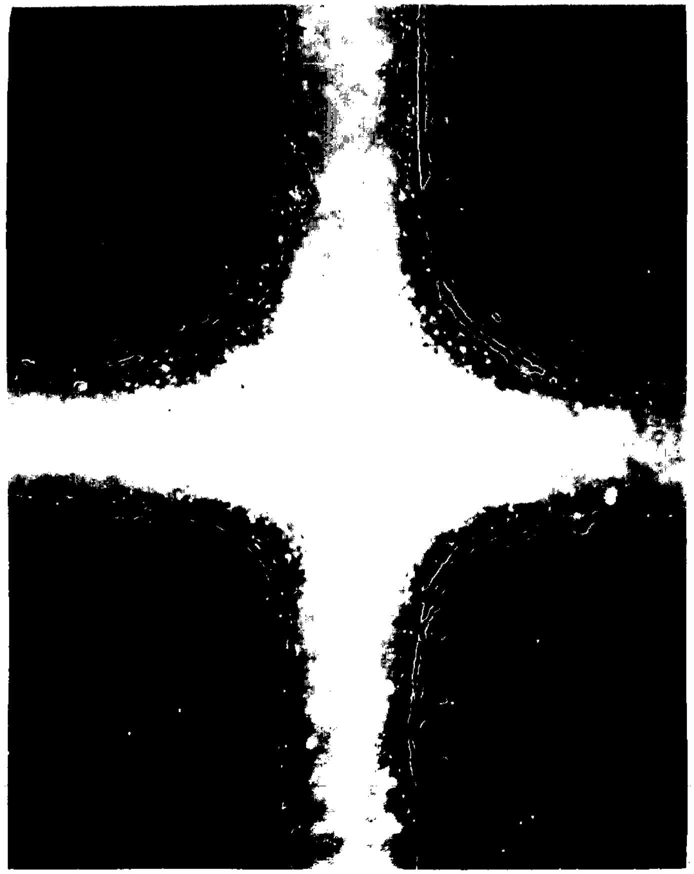
VEHICLE CATALYST	CONTAMINATES PB	S	P	ZN	MN	CA	CL	CU
MMT-BK9I	.1215	.0000	.2145	.1476	.9821	.0114	.0000	.0325
MMT-BK9M	.0649	.0000	.0907	.0302	.5311	.0041	.0000	.0249
MMT-BK9O	.0505	.0000	.0692	.0178	.4021	.0080	.0000	.0241



1988 SABLE
3.0L ENGINE
27,416 MILE

1988 3.0L Sable- 27,416 Miles

Inlet



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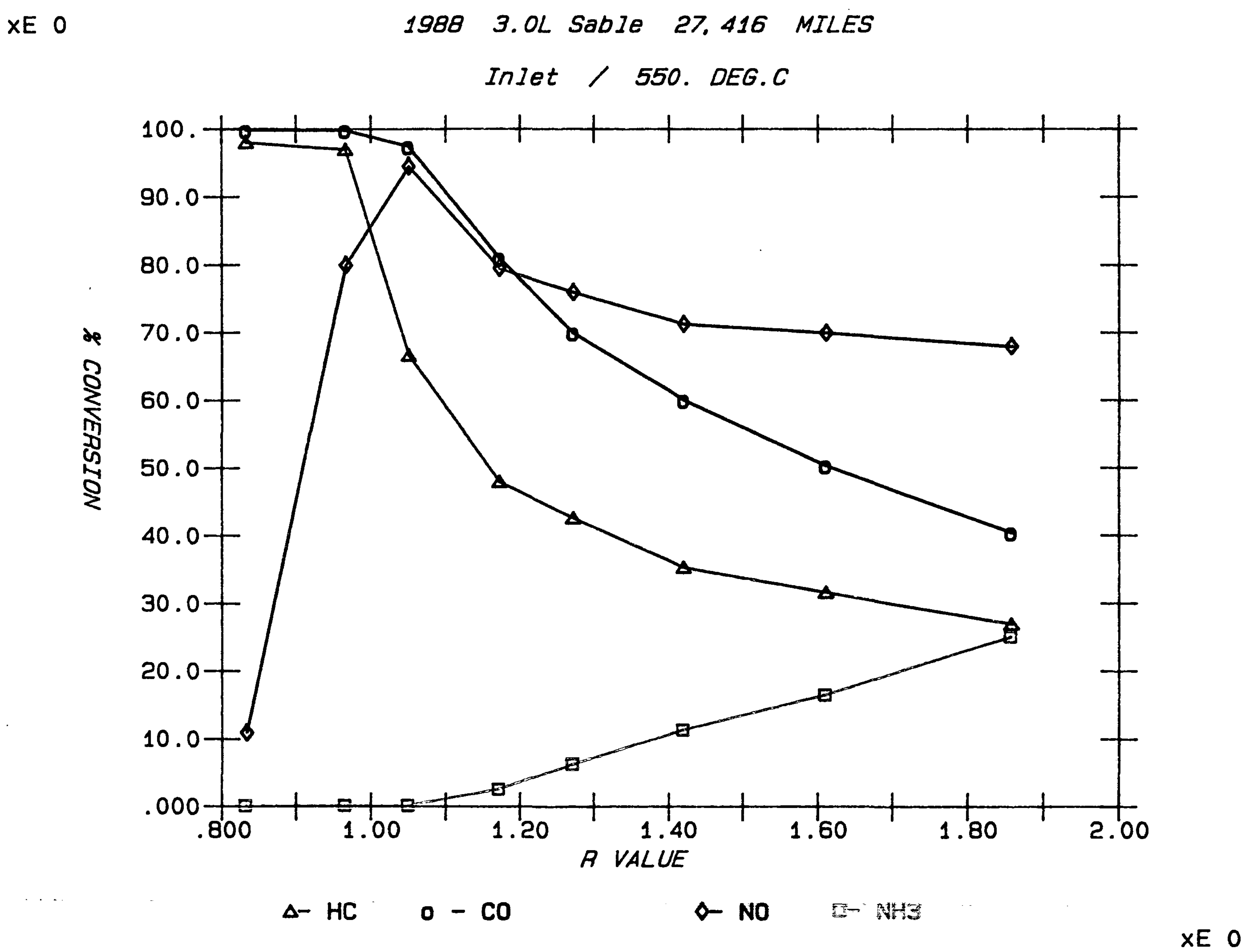
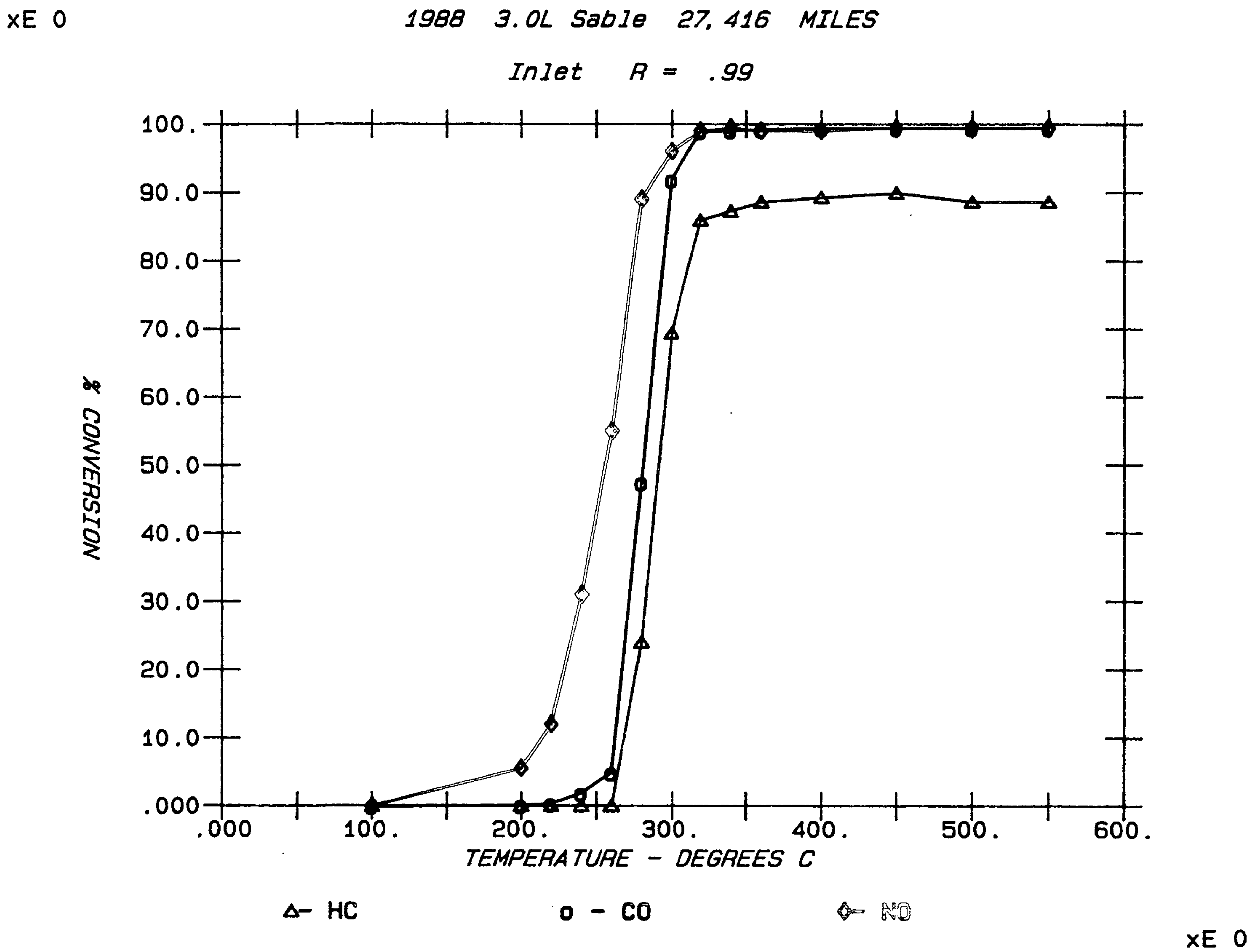

xE 0
1988 3.0L Sable 27,416 MILES
Inlet / 550. DEG.C
% CONVERSION
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
Δ- HC
o - CO
◇- NO
□- NH3
xE 0


xE 0
1988 3.0L Sable 27,416 MILES
Inlet R = .99
% CONVERSION
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
△- HC
o - CO
◇- NO
xE 0

Appendix J

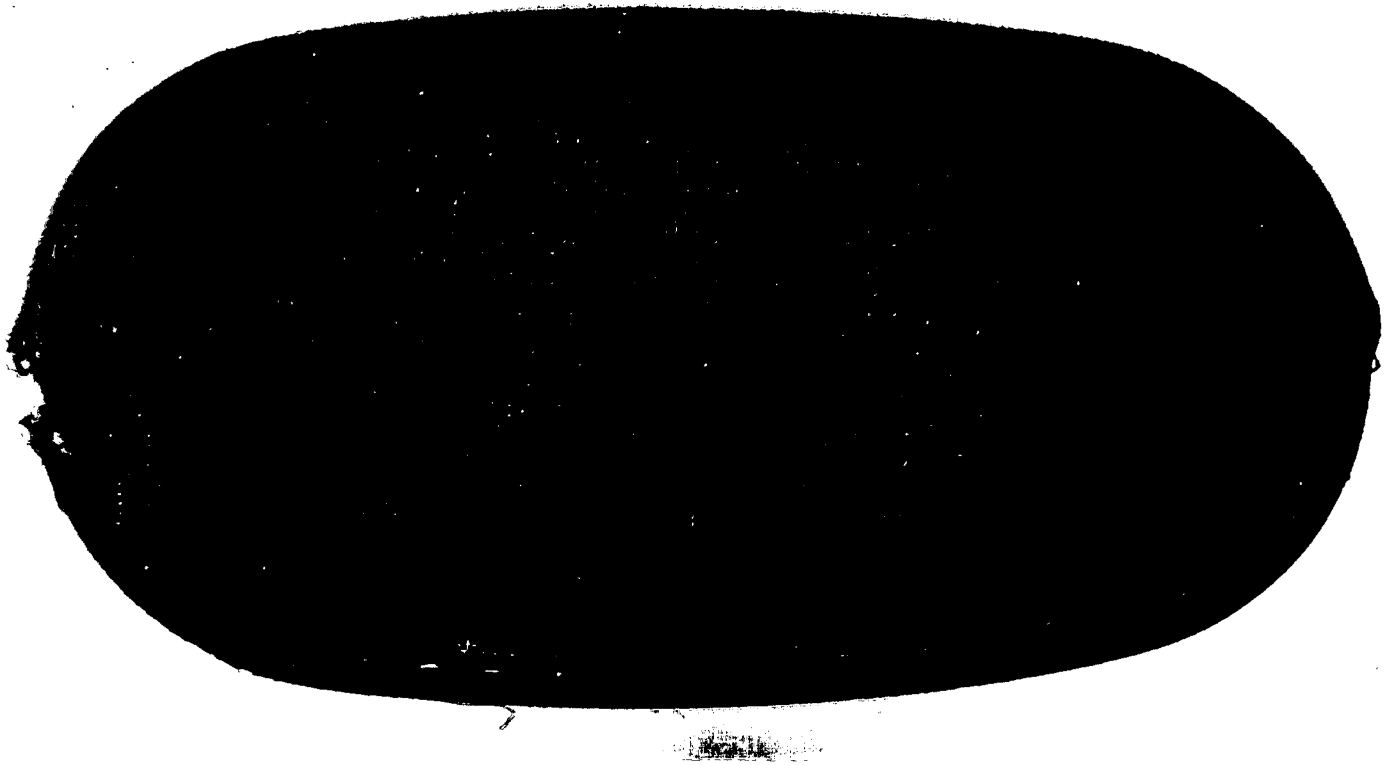
1988 3.0L Taurus

39,662 Miles

X-RAY FLUORESCENCE ANALYSIS OF MMT CATALYSTS

VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) CATALYTIC COMPONENTS PT	RH	PD	NI	CE	BA	LA	FE	g/ft^3	Pt/Pd/Rh
1988 3.0L Taurus		**39,662 Miles**									
MMT-BK10I	21.9	.2083	.0415	.0000	.7752	5.5875	.7679	.2161	.2927	36.5	5.0/0/1.0
MMT-BK10M	18.8	.1904	.0381	.0000	.7462	5.6083	.6995	.2183	.2898	33.4	5.0/0/1.0
MMT-BK10O	17.2	.1910	.0371	.0000	.7109	5.6701	.7052	.2248	.2905	33.3	5.1/0/1.0
									Average:	34.4	5.0/0/1.0

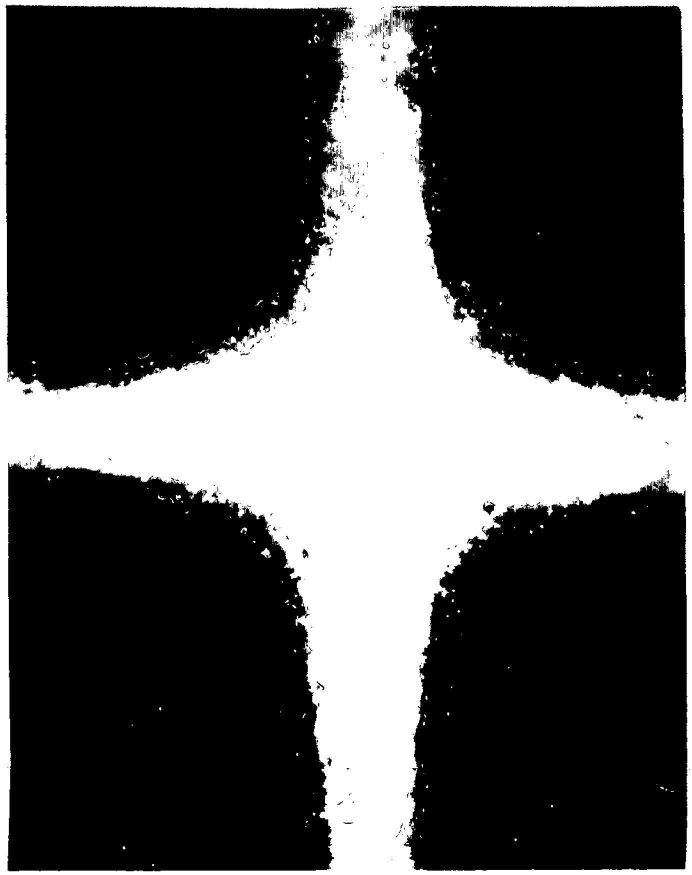
VEHICLE CATALYST	CONTAMINATES PB	S	P	ZN	MN	CA	CL	CU
MMT-10I	.1262	.1277	.0818	.0888	.7912	.0077	.0000	.0242
MMT-10M	.0309	.0964	.0509	.0189	.5221	.0000	.0000	.0222
MMT-10O	.0180	.0683	.0413	.0141	.4419	.0000	.0000	.0221



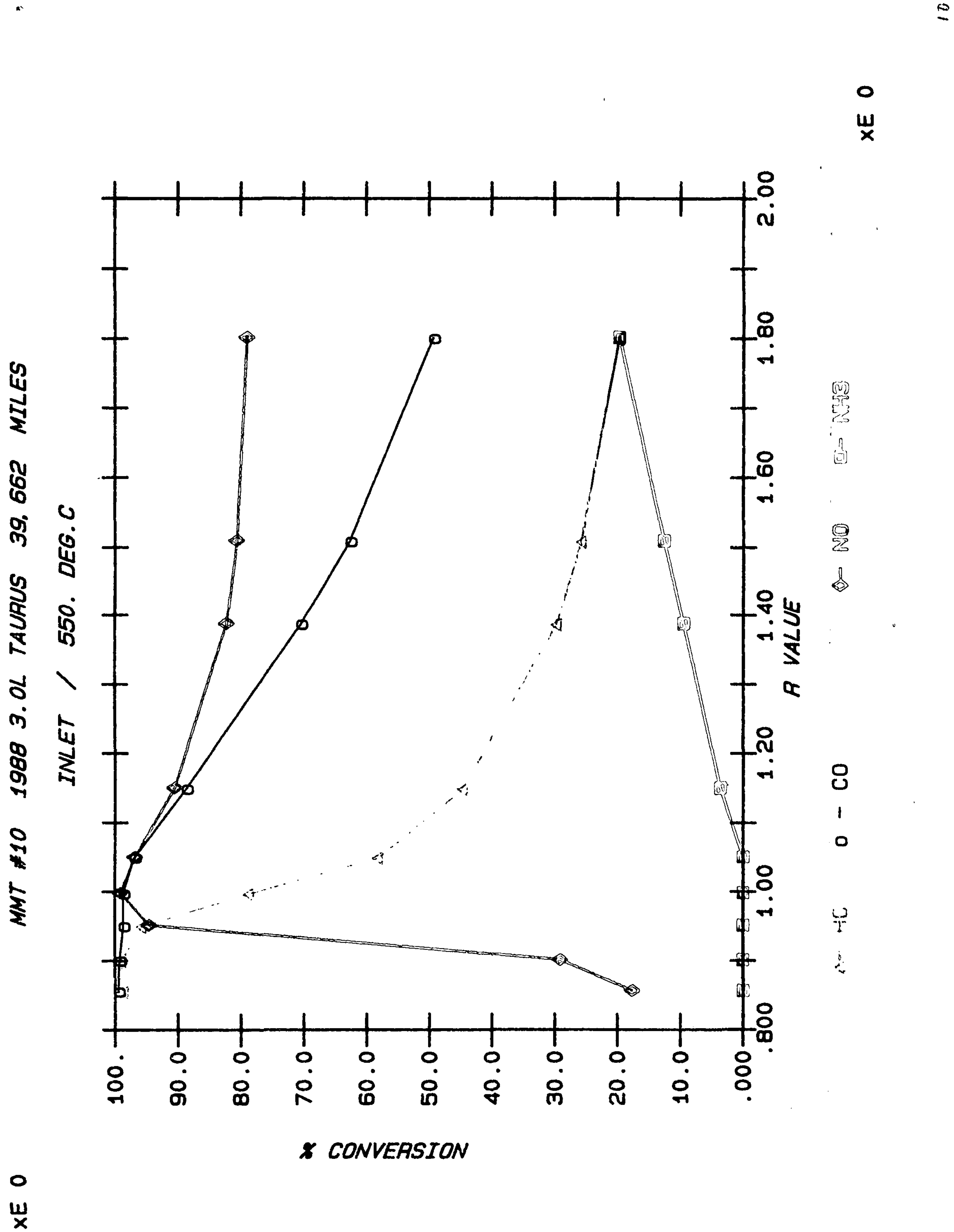
1988 TAURUS
3.0L ENGINE
39,662 MILE

1988 3.0L Taurus- 39,662 Miles

Inlet

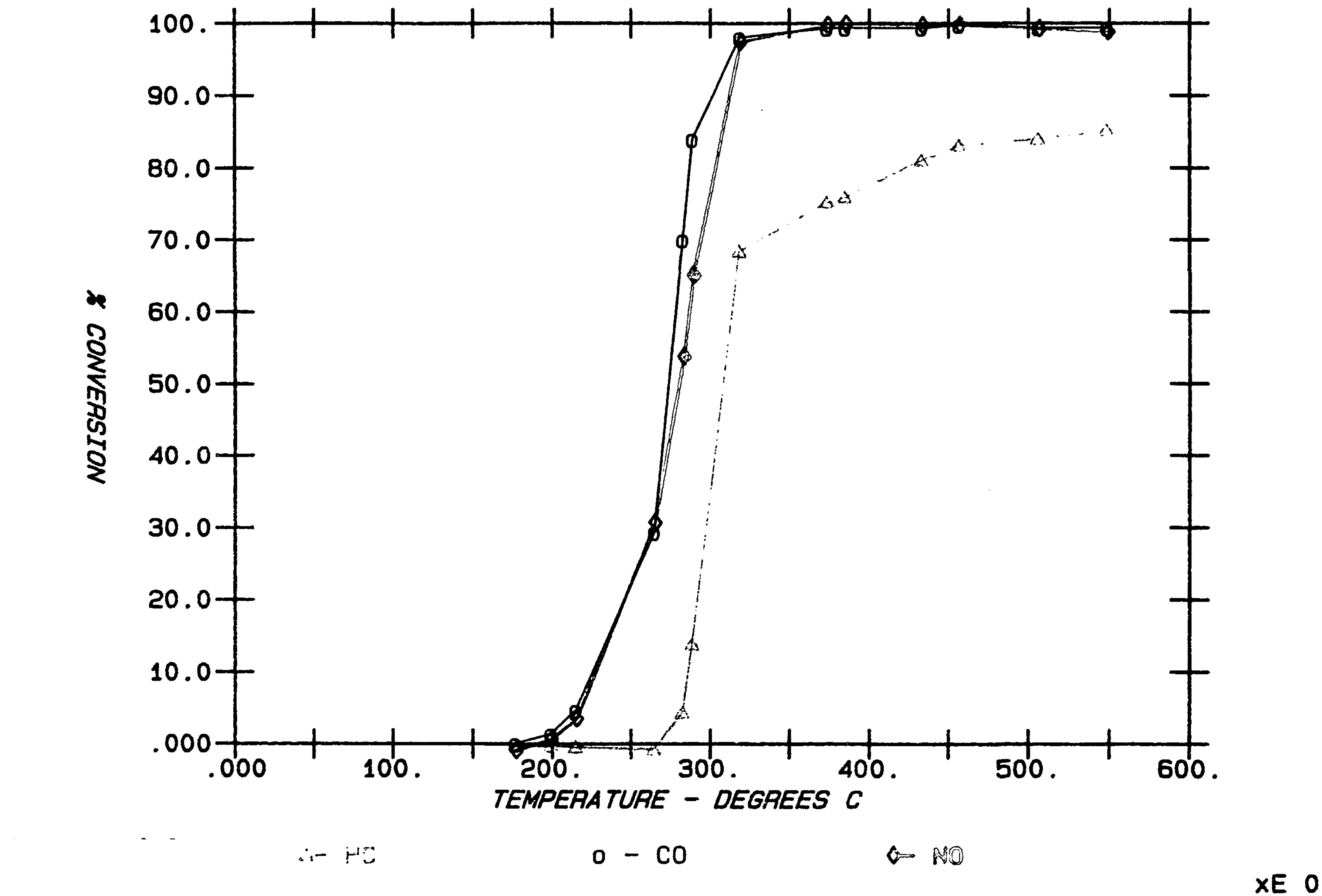


80X


MMT #10 1988 3.0L TAURUS 39,662 MILES
INLET / 550. DEG.C
% CONVERSION
R VALUE
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.800
1.00
1.20
1.40
1.60
1.80
2.00
xE 0
xE 0
HC
O - CO
NO
NH3

MMT #10 1988 3.0L TAURUS 39,662 MILES

INLET R = 1.00



Analysis Results of 41 Canadian Catalysts

Effect of MMT on Catalysts
Vehicles Evaluated for Effects of MMT

Model	Miles	Type	BET(m2/g)	Mn (wt%)
Bronco II	13,545	TWC	15.5	2.62
Bronco II	13,545	COC	21.5	1.00
Bronco II	16,585	TWC	13.5	2.47
Bronco II	16,585	COC	24.4	1.36
Lynx	22,000	TWC	0.8	0.79
Lynx	22,000	COC	0.3	1.62
Tempo	22,000	TWC	7.3	4.20
Tempo	22,634	TWC	xxxx	3.13
Tempo	22,634	COC	xxxx	0.81
Topaz	24,000	TWC	13.9	1.43
Topaz	24,000	COC	7.6	0.48
Lynx	26,971	TWC	1.0	2.40
Lynx	26,971	COC	8.9	1.88
Bronco II	27,992	TWC	8.3	4.75
Bronco II	27,992	COC	4.3	2.25
Escort	28,000	TWC	4.4	1.77
Escort	28,000	COC	6.9	1.76
Topaz	28,000	TWC	14.1	3.15
Ranger	28,945	TWC	2.9	4.93
Ranger	28,945	COC	xxxx	2.48
Merkur	32,000	TWC	8.9	1.72
Merkur	32,000	COC	8.4	0.81
Escort	32,319	TWC	10.5	4.85
Escort	32,319	COC	3.4	2.87
Ranger	33,000	TWC	3.8	6.14
Ranger	33,000	COC	1.2	3.39
Aerostar	33,670	TWC	15.0	2.72
Aerostar	33,670	COC	16.4	1.57
Tempo	34,000	TWC	8.5	5.20
Escort	35,776	TWC	11.7	2.34
Escort	35,776	COC	2.7	1.98
Taurus	39,338	TWC	23.3	0.21
Taurus	39,338	COC	18.2	0.04
Bronco II	43,000	TWC	3.8	2.08
Bronco II	43,000	COC	2.7	0.83
Mustang	44,740	TWC	4.5	6.30
Mustang	44,740	COC	1.6	1.82
Tempo	47,149	TWC	2.0	4.82
Tempo	47,149	COC	0.6	2.73
Bronco II	49,467	TWC	9.0	4.89
Bronco II	49,467	COC	xxxx	xxxx

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ATTACHMENT 4

"RESULTS OF COORDINATING RESEARCH COUNCIL
MMT FIELD TEST PROGRAM" (SAE 790706)

ATTACHMENT 2

FORD REPORT:
ANALYSIS OF 26 CATALYSTS FROM CANADIAN VEHICLES

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IV-D-59

Inter Office

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May 10, 1989

To: R. Bright
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Subject: **Effect of MMT on Catalysts.**

Summary

A second series of 26 catalysts removed from Canadian vehicles have been characterized. The results indicate that the combustion product of MMT, Mn_3O_4, is the primary mechanism for the decreased efficiency of the catalysts characterized in this study. The results show that a 5-30 micron thick layer consisting of Mn_3O_4 exists on the washcoat and contributes physically to the deterioration of the efficiency of the catalyst. This layer in effect increases the mass transfer resistance and thus decreases the efficiency to promote conversion of HC, NO_x and to a lesser degree CO. Data from this series show that as the Mn concentration increases the conversion of HC and NO_x decreases. Similarly, light off temperature increases as the concentration of Mn increases. Analytical results for this series show the inlets of catalysts to have between 0.21 and 6 wt% Mn. Contaminants such as Pb, S, P, and Zn did not contribute to the reduced catalyst efficiency. Reduction of 10 and 30% was observed in conversion efficiency for both HC and NO_x. Sufficient data was not available to draw a definite conclusion as to whether or not the MMT effects were localized as to a specific Canadian Province. Although, the trend of the data shows that the Province of Quebec has the highest incidence. An open issue of the effect MMT on other emission components remains. This data supplements and confirms earlier work (1,2) on the effects of MMT on catalysts.

Background

Earlier work on MMT (1,2) covered the results of the characterization of nine converters, a total of 15 catalysts, that had extensive exposure to the fuel additive MMT. The following results were summarized in those reports.

- Minor to severe plugging of the inlet brick by the Mn_3O_4 residue.
- A 5-30 micron thick layer of Mn_3O_4 covered the washcoat.
- Lower than normal surface area (BET).
- Percent conversion of HC, CO and NO_x decreased as the exposure to MMT increased.
- Light-off temperature for HC, CO and NO_x increased as the exposure to MMT increased.
- NH_3 formation increased as the exposure to MMT increased.

Based on these results it was concluded that the MMT fuel additive had a deleterious effect on catalyst efficiency. In addition these results were presented at the SAE International Congress and Exposition in February 1989 as paper SAE 890582.

An additional series of 13 converters (total of 26 catalysts) have been received and have undergone similar characterization. These catalysts, accumulated mileage, and their source locations are shown in Table 1. For comparison the source locations for the first series are shown in Table 2. The second series have mileage accumulation in the range of 13,545 to 44,740 miles and an average of 32,240 miles as compared to 22,000 to 43,000 miles and an average of 29,000 miles for the first series.

Table 1

Source of Canadian Catalysts - Series 2

Sample	Mileage	Location
100	22,634	Pointe Claire, Quebec
101	35,776	Dartmouth, N. S.
102	47,149	St-Leonard, Quebec
103	49,467	Airdrie, Alberta
104	32,319	St-Leonard, Quebec
105	26,971	Quebec City, Quebec
106	39,338	Thunder Bay, Ontario
107	27,992	Ville D Anjou, Quebec
108	44,740	Scarborough, Ontario
109	16,585	London, Ontario
110	28,945	Vanier, Quebec
111	13,545	Vanier, Quebec
112	33,670	Hamilton, Ontario

Table 2

Source of Canadian Catalysts - Series 1

Sample	Mileage	Location
301A	43,000	Fort St. John, BC
301B	24,000	Lachine, Quebec
301C	34,000	Lachine, Quebec
301D	22,000	Montreal, Quebec
301E	28,000	Verdun, Quebec
301F	28,000	Point Claire, Quebec
301G	22,000	Grand Falls, NFLD
301H	32,000	Ontario
301I	33,000	Lachine, Quebec

As with the first series, the converters for the second series were removed from vehicles that had been returned to Canadian dealerships for poor performance and driveability problems. Under warranty the converters were removed and subsequently shipped to Research for post mortem characterization. No additional information concerning the driving or fueling characteristics for these vehicles were transmitted with the catalysts. Again, the assumption was made that these vehicles were maintained and fueled with fuel containing the Canadian specification for MMT, 16.7 mg/l.

Results and Discussions

This series of converters consisted entirely of the 2 brick catalyst system. Visually, the as-received condition of each catalyst was examined and photographs are shown in **APPENDIX A**. With the exception of two converters all bricks were intact as canned. The two exceptions were identified as #100 and #103. The former (#100) showed exposure to severe over-temperature conditions and the rear portions of bricks 1 and 2 were melted and broken. The latter (#103) had undergone severe abrasion conditions and was reduced to a single brick of baseball size. Converter #106 apparently was mislabeled as having 33,000 miles, the converter housing was only slightly discolored and the bricks did not appear to be covered with the reddish residue characteristic of those exposed to MMT containing fuel. As with the first series each brick in this series was covered with a rust colored residue. In contrast, plugging of the inlet channels was minor to severe in the first series, it was not as prevalent in the second series.

The results of x-ray fluorescence analysis of samples taken from each catalyst are shown in Table 3. These results confirm the first brick to be Pt/Rh with a nominal ratio of 5:1 and the second brick to be Pt/Pd with a nominal PM ratio of 1:1. Exceptions being the first brick of #104 which had a calculated PM ratio of 12:1 and the <u>second</u> bricks from converters #109 and #111. These bricks were identified as Pd/Rh with a nominal PM ratio of 5:1. From the XRF data the calculated PM loadings ranged between 8 and 32 g/ft^3. The lower PM loading and precious metal content from #108 indicated a possible loss of PM from the washcoat. Nominal PM loading are

20 to 28 g/ft^3 and with the exception of #108 these catalysts fall within acceptable limits. The Mn concentration ranged between 0.21 and 6.3 wt%. The lower observed value of 0.21 wt% was from #106 which was apparently mislabeled as to mileage. Contaminant levels of S, P, and Zn were at or below the detection limits of the analytical method (XRF) used for analysis. Lead concentrations in excess of calculated nominal retention levels were present on catalysts #102 (1.6 wt%), #103 (1.3 wt%), and #107 (1.4 wt %). These vehicles may have been misfueled during in-use service.

X-Ray diffraction analysis of samples from vehicles with accumulated mileage in the ranges of 10K to 40K, 21K to 30K, 31K to 40K, and 41K to 50K showed that samples #107, #108 and #109 had the α-alumina phase present. This α-phase indicates that these catalyst had undergone exposure to temperatures >1000° C at some time during their operation. Sample #112 from the 31-41K mileage range did not show the α-alumina phase present. X-Ray diffraction analysis also confirms the rust colored residue to be Mn_3O_4.

BET surface activity measurements on the second series (Table 3) range between 1.25 and 22.56 m^2/g for the first brick and between 0.61 and 21.61 m^2/g for the second brick. Catalysts #100, #108, and #110 have BET values below 5 m^2/g which indicates their exposure to operating temperatures greater than 1000° C. These values confirm the XRD results. Catalyst #103 had only one brick which had been abraded to the size of a baseball but still had a BET value of 9 m^2/g. In comparison, in-use vehicles having BET's greater than 5 m^2/g are considered acceptable and BET's for fresh catalyst fall in the range of 25 m^2/g.

Optical micrographs from selected catalysts are shown in **APPENDIX C**. These samples were taken from catalysts in the different mileage categories of 10K-20K, 21K-30K, 31K-40K, and 41K-50K miles. Most evident in each micrograph is a layer covering the washcoat. It's estimated thickness varies between 5 and 30 microns. In order to identify and measure accurately the thickness of the layer in relation to the washcoat, scanning electron photomicrographs were taken from each of these samples. These photomicrographs are also contained in **APPENDIX C**. Energy dispersive x-ray analysis identified the layer as containing high concentrations of Mn. In addition, an elemental distribution x-ray maps of Al is also shown in **APPENDIX C**. X-Ray distribution maps of P, S, and Pb were not obtained because of their low concentration. Using the Mn elemental distribution and the photomicrographs, the measured thickness of the Mn layer on the washcoat varies between 5 and 30 micron. The thickness of washcoat of the catalyst generally falls in the range of 10 to 30 microns.

Conversion efficiencies for HC, CO, and NO_x were measured for all of the catalysts in this series. The results, % conversion at R = 1.00 are summarized in Table 4. For reference the table includes vehicle model, model year, engine type, mileage accumulated, and both the wt% of Mn and Pb. Curves for both light-off and steady state R are shown in **APPENDIX B**. The HC conversion efficiency varies between 28 and 99% for catalysts having between 6.3 and 0.21 wt% of Mn. Similarly, NO_x conversion varies between 9 and 95 % for catalysts having between 6.3 and 0.21 wt% Mn. Shown in figure 1 is a plot using data from Table 4. In order to eliminate the effects of thermal deterioration and of any Pb contamination on the conversion efficiency, data from those affected catalysts were not included in the plot. Data from the first series was included using the same criteria. The results show that as the percentage of Mn increases the conversion efficiency for both HC and NO_x decreases. Light-off efficiencies for HC, CO and NO_x were also measured for all of the catalysts in this series. The results, shown in figure 1 for temperature at 50% conversion, indicate that as the percent manganese increases the temperature at 50% conversion for HC and NO_x increases. In both the conversion efficiency and light-off curves the effects of the Mn_3O_4 layer is evident with the decreased activity for both HC and NO_x.

In order to determine if Mn could be tolerated at a lower level, the concentration of Mn versus the percent conversion of both HC and NO_x was plotted using selected data from the second series of catalysts. The data was selected on the basis of low levels ($\leq$1%) of contaminants such as Pb, P, Zn and surface activity (BET) was >5 m^2/g. The resulting plot (figure 1) shows that as the concentration of Mn increases the percent conversion decreases. Conversion efficiency of 85% for both HC and NO_x is reached at approximately 1.5% Mn. A similar plot of temperature at 50% Conversion versus % Mn shows that as the percent of Mn increases the temperature also increases.

TABLE 4

CONVERSION EFFICIENCIES FOR HC, CO, AND NO_x SERIES 2

Sample Number	Vehicle Model	Engine	MY	Mileage	Weight % Pb	Weight % Mn	% Conversion (R=1.00) HC	% Conversion (R=1.00) CO	% Conversion (R=1.00) NO_x
100	Tempo	(2.3L)	1984	22,634	0.06	3.13	51	95	22
101	Escort	(1.9L)	1987	35,716	0.16	2.34	72	95	75
102	Tempo	(2.3L)	1984	47,149	1.60	4.82	28	87	9
103	Bronco II	(2.8L)	1984	49,467	1.30	4.89	74	99	34
104	Escort	(1.9L)	1986	32,319	0.20	4.85	74	96	30
105	Lynx	(1.9L)	1986	26,971	0.01	2.40	82	98	85
106	Taurus	(2.5L)	1987	39,330	0.02	0.21	99	99	95
107	Bronco II	(2.8L)	1985	27,992	1.39	4.75	68	98	60
108	Mustang	(2.3L)	1985	44,740	0.44	6.30	61	91	68
109	Bronco II	(2.9L)	1987	16,585	0.15	2.47	78	99	95
110	Ranger	(2.8L)	1985	28,945	0.60	4.93	73	99	58
111	Bronco II	(2.9L)	1987	13,545	0.02	2.62	90	99	87
112	Aerostar	(3.0L)	1987	33,670	0.12	2.72	70	99	88